OPTIMAL SELECTION AND DESIGN OF A METHANOL PROCESS WITH ENHANCED CO_2 UTILIZATION

A Thesis

by

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ABSTRACT

The recent discoveries of significant reserves of shale gas have spurred various monetization pathways including the production of methanol. There are several routes to convert shale/natural gas to methanol. The decisions for technology selection and process design were typically based on techno-economic criterial. Because of the growing interest in reducing the greenhouse gas emissions of gas processing, carbon footprint is emerging as a primary criterion in the selection and design of the process. The purpose of this work is to carry out process synthesis, selection, and design of a shale-gas to methanol process with multiple objectives including profitability and carbon footprint. Several reforming pathways along with the associated downstream processing are considered. In addition to the screening of individual types of reforming, the study also considers combined reforming of methane which incorporates three types of reforming, namely steam reforming, partial oxidation, and dry reforming. It is desired to consider existing technologies and to also modify the design of an existing methanol technology to include combined reforming. Utilization of CO_2 is addressed while maintaining the suitable syngas ratio for methanol synthesis, and minimizing CO_2 emissions, waste water generation, and energy requirements of the overall process. A methanol from natural gas production plant with a capacity of processing 280 MMSCFD is considered as the base case scenario. The plant employs conventional reforming (e.g. steam reforming, partial oxidation, or ATR) to generate syngas for methanol synthesis. Aspen HYSYS is used to simulate the process scenarios and SWROIM is used to aid determining the ultimate reforming configuration based on economic and sustainability indicators. Heat and power integration are performed to improve the sustainability and profitability of the process, through identifying water and heat sinks in the overall design. A techno-economic analysis of the proposed designs are conducted, including the fixed capital cost, carbon taxes, and utility requirements. Sensitivity analysis of each proposed design is carried out to assess the impact of natural gas and methanol prices on the profitability. Additionally, sensitivity analysis is performed to evaluate the effects of imposing carbon tax and carbon credit regulations.

Keywords: syngas, carbon footprint, integration, design, sustainability.

DEDICATION

To the memory of a leading scholar, a stalwart educator and a caring mentor, Prof. Sam Mannan.

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1. INTRODUCTION AND BACKGROUND

The shale gas discoveries in recent years have encouraged innovation and technology developments (1). One profitable pathway to convert the shale gas into an added value chemical, such as methanol. Methanol is a key component to a vast number of chemicals (2) such as formaldehyde, acetic acid, dimethyl ether, etc. The global demand for methanol has been steadily increasing since the first methanol commercial plant in 1960 in Germany. The current global methanol need is estimated to be over 80 million metric tons, which is double the methanol demand in 2006. According to IHS in 2016, methanol demand market is expected to be almost 100 million metric tons by 2020 (3).

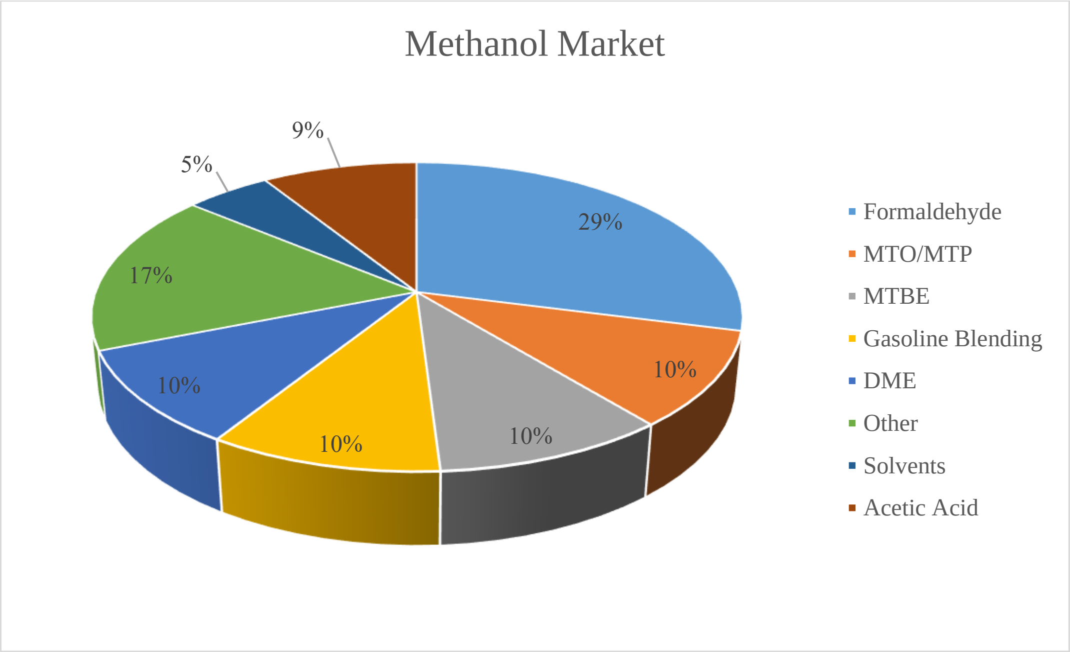


Figure 1 Methanol demand by end use (Reprinted from IHS (3))

In order to produce methanol, the shale/natural gas goes under catalytic reforming where syngas at a certain ratio is produced, the syngas is then sent to a reactor where crude methanol is synthesized. The generation of syngas is an extensive energy process (4), the conventional methods used are either by using steam reforming, partial oxidation or a combination of both. In steam reforming, the reformer operates at high temperature >700 ^{o}C (5), natural gas is usually used as fuel to supply heat to the reactor, this method of providing energy generates a large amount of flue gas containing CO_2. For the cases where partial oxidation or auto-thermal reforming options are chosen, heat maybe produced or the reformer could be thermally balanced. The feed that is supplied to POx is reacted with high purity oxygen (6), oxygen is supplied by an external air separation unit. Oxygen processing requires a large amount of energy for the separation of oxygen from air, thus emitting CO_2. In addition, the costs of the reforming unit in a methanol plant represents around 60% of the overall plant cost (7). The use of the aforementioned conventional technologies leads to increasing the greenhouse gases, namely CO_2 in the atmosphere. The process of methanol production has gone under a series of developments, starting from improving the operating conditions of the methanol reactor, to catalyst development and expanding the reforming options of the natural/shale gas to produce syngas. Yet, the reformer unit is considered the most energy extensive step among the methanol production train, thus accounting for the majority of the costs associated with the methanol plant (7, 8).

In recent years, it has become a desire to utilize waste, specifically CO_2 as a feedstock and a source of carbon for fuels and chemicals, to improve the economic and environmental aspects of the process. Song (9) proposed the new process of tri-reforming, where three types of reforming are combined in one. The three types are steam reforming of methane (SRM), Partial Oxidation of Methane (POx) and Dry Reforming of Methane (DRM), where the latter employs CO_2 and methane as the primary feedstock. This combination overcomes a number of issues that are associated with the single reformer options (9, 10), the combined reforming can (i) produce the desired ratio of syngas (ii) prevent the catalyst deactivation caused by carbon formation (iii) reduce issues associated with the formation of hot spots on the catalyst. Also, there is no need to pre-treat the CO_2 obtained from the power plant flue gas the (9). Noureldin et al. (11) presented and developed an equilibrium model that takes into account the economics, energy and environmental aspects. In addition to the aforementioned benefits, the employment of combined reforming reduces the carbon footprint (12, 13). Challiwala et al. conducted a combined thermo-kinetic study investigating different scenarios for combined reformer. The scenarios include the effect of equilibrium temperature and pressure, addition of steam, addition of oxygen and the simultaneous addition of steam and oxygen. They determined the optimal feed compositions and conditions for the reformer with 47.8% conversion of CO_2 in the reformer. A techno-economic assessment was conducted by Julian-Duran et al. (13) examining all the conventional reforming options along with combined reforming, showing that ATR and POx had the highest economic potential, while CR had the lowest carbon footprint. Some work have been done in the area of flue gas compositions, Minutillo and Perna (14) studied the impact of different flue gas compositions on the quality of syngas composition as well as CO_2 emissions. They were able to determine the optimum operating conditions of the reformer for different types of flue gasses compositions as well as reducing CO_2 emissions by 83% for flue gas from a power plant that utilizes natural gas as fuel and 84% for a flue gas coming from a power plant that utilizes coal as fuel. The same authors also extended their study (15) to include methanol synthesis part, where they emphasized on the significance and importance of flue gases compositions containing low concentrations of oxygen. Ng et al. (16) investigated the economic feasibility of different cogeneration process combinations with either

CO_2 storage or utilization. They highlighted the techno-economic improvements when CO_2 is being utilized and converted into methanol through combined reforming rather than storing the CO_2. Zhang et al. (17) developed a flowsheet for the production of methanol from methane and CO_2 via combined reforming, as well as performing heat integration to reduce the costs of the process. They also highlighted the differences between combined reforming and steam reforming in terms of energy requirement and methanol production. Dwivedi et al. (18) modified the flowsheet that was developed by Zhang et al. (17) in order to improve the process outputs. They performed two major modification that resulted in four different scenarios. The first modification was adjusting the reformer pressure in order to reduce the reactor volume. The second change was installing a water separation unit after the reformer to eliminate water prior to the methanol synthesis section since water reduces the catalyst activity (19-21) thus lowering methanol conversion.

The purpose of this study is to enhance the economics and environmental aspects of an existing methanol plant through process synthesis, selection, and design. CO_2 is utilized as a feedstock for the production of syngas. Different shale gas reforming options are screened, investigated and modified to determine the optimal design of the reforming unit. Mass and energy integration analyses are performed through identifying water and heat sinks to enhance the sustainability and to make the process economically attractive. Aspen HYSYS is used to simulate the process flowsheet, SWROIM is used to determine the ultimate configuration option based on economic and sustainability indicators. A detailed economic analysis is performed, including the fixed capital investment, carbon taxes, and energy requirements.

2. PROBLEM STATEMENT

An existing methanol production plant with a capacity of processing 280 MMSCFD of shale gas, utilizes a conventional reforming technology to produce syngas. It is desired to retrofit the plant by including other forms of reforming (e.g., dry reforming) to reduce carbon footprint, and to increase the profitability and the sustainability of the process. In additions, determine the impact of the fluctuations of shale gas and product prices. The effect of carbon tax and carbon credit is addressed.

2.1 Objectives

- Maintain the desired syngas ratio and stoichiometric number at the levels that are suitable for methanol synthesis
- Perform economic analyses on the final designs to determine the feasibility of the each proposed reforming design
- Identify mass and energy integration opportunities in the process that arise from produced flowsheets
- Assess sustainability of the final proposed designs

3. METHODOLOGY

A methanol plant that utilizes conventional reforming technology (e.g. steam reforming, partial oxidation, etc.) as the primary source for syngas is considered for modifications, where other forms of syngas production are incorporated in the design, to enhance CO_2 utilization while maintaining the desired syngas ratio required for methanol synthesis. Several designs for methanol production using different reforming pathways are proposed and evaluated from an economic and environmental prospective. The considered reforming technologies in this study includes Partial Oxidation (POx), Dry Reforming (DRM), a combination of steam reforming and partial oxidation which is known as autothermal reforming (ATR), and a combination of steam, partial oxidation and dry reforming which is referred to as Combined Reforming (CRM). The approach is divided into five major steps (i) preliminary screening of conventional methanol plants including the syngas production unit (ii) flowsheet simulation using Aspen HYSYS and the validation of the flowsheet (iii) flowsheet modification where one or more of the aforementioned technologies are involved in the production of syngas (iv) mass and heat integration (v) comprehensive economic and environmental assessment of each proposed scenario and give recommendations.

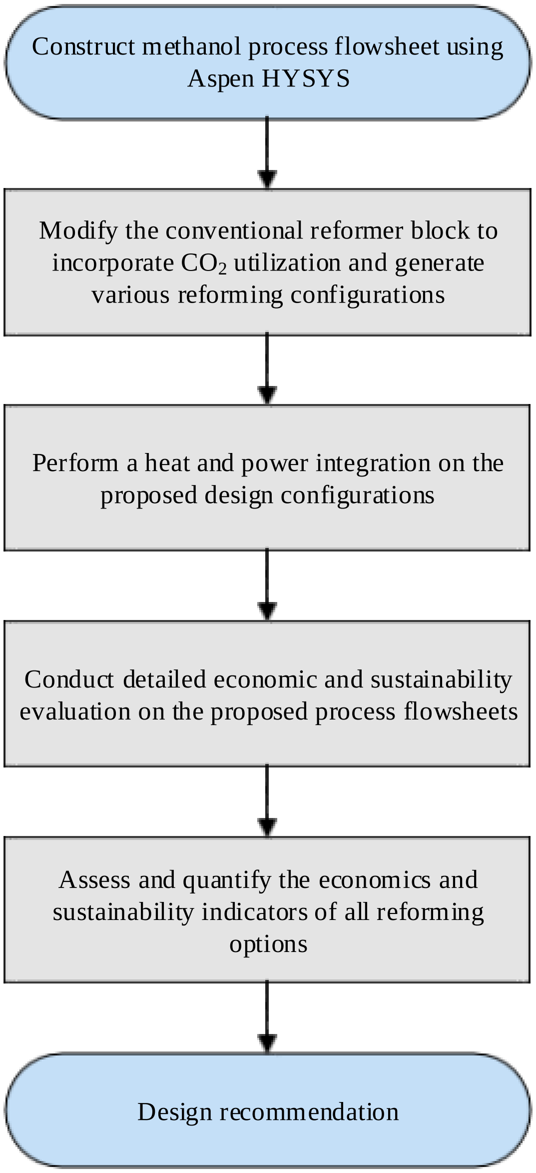


Figure 2 *Flowchart showing the approach*

3.1 Preliminary Screening of conventional Technologies

The production of methanol from natural/shale gas starts by removing impurities such as hydrogen sulfide (H_2S). The next step is reforming, where syngas is produced, depending on the process conditions and reforming option, if the syngas is produced at the desired ratio then no conditioning step is needed. However, if the syngas ratio is more/less than the desired ratio, then the conditioning step is required (e.g. WGS). Once the obtained syngas has the desired ratio, the feed is compressed and fed to a methanol converter, where crude methanol is produced. Finally, methanol is purified to produce grade product methanol through the use of distillation.

In this Overview, various reforming and syngas production routes are introduced and discussed in depth along with most common commercialized technology to convert syngas to methanol.

3.1.1 Feed Pretreatment

The shale gas compositions is assumed to be fixed with the conditions and compositions shown in Table 1. In this study it is assumed that the natural gas id already processed and the feed is free from Hydrogen Sulfide (H_2S), in cases where H_2S is present, a desulfurization unit should be installed to prevent H_2S from poisoning and deactivating the catalysts in the reformer or in the methanol converter. The feed shown in Table-1 is rich with methane and contains only small fractions of C_2 and C_3, therefore a pre-treatment unit is required, where higher hydrocarbons are being transformed into syngas.

Table 1 *Mean gas compositions entering the reformer (Reprtinted from (22))*

Component	**% (moles)**
CH_4	93.12
C_2	3.20
C_3	0.70
CO_2	1.21
N_2	1.37

3.1.2 Reforming

The pre-treated gas is then sent to a steam reformer where the production of syngas takes place. As mentioned above, the energy consumption of the reformer unit is generally high, which results in emitting large quantities of CO_2 through flue gas. To overcome the large energy requirements, some commercialized methanol technologies combine two types of reforming where endothermic and exothermic reactions are carried out in either one or two reactors, these two reactions are SMR and Partial Oxidation of Methane (POx). The combination where SMR and POx are combined in one reactor is called Auto-Thermal Reforming (ATR) and is used to offset the extensive energy required by SMR, since POx produces heat as the reaction proceeds. In most cases where ATR is used the reactor can sustain the required energy from the exothermic reaction. Although ATR may not require an energy output, a great deal of energy have been already consumed in order to separate the high purity oxygen from air in the Air-Separation-Unit (ASU), before it is being sent to the reformer (23). Another distinguished type of reforming is called Dry Reforming of Methane (DRM). Although DRM uses CO_2 as feedstock the net carbon emission is positive, since the reaction is highly endothermic and requires a massive amount of energy in order for the reaction to be favored. An additional drawback of DRM usage in a methanol plant is the poor syngas quality that is obtained from DRM.

In some plant designs, a secondary reactor is added to aid in the primary reformer in converting the feed into syngas and to help prevent coke formation (4). The secondary reactor could be installed before (pre-reformer) or after (post reformer). In the case of pre-reformer, higher hydrocarbons are converted into methane in a lower temperature than that of regular reformer due to the relative simplicity of breaking the bonds of higher hydrocarbons, the hydrocarbon reactivity has been suggested as follows (24):

Cyclohexane > trimethylbutane > n-butane & n-decane > n-heptane > ethane > benzene > methane

The post reformer converts the methane residuals thus reducing the cost through increasing the capacity. Another technique to increase the capacity of the primary reformer is to recover the heat from the effluent stream via preheating primary reactor feed. An important variable of the process is the Steam-to-Carbon ratio or S/C, which has a significant impact on the carbon formation on the catalyst surface (4).

As mentioned above, there are multiple options to choose from for the reforming of natural/shale gas. There is no best route to produce syngas. However, there are practical routes and designs which depend on the project needs and the available resources (5). Typically, a nickel based catalyst is used for in the reformer (4). Each reforming type produces a certain syngas ratio that is characterized by the following formulas:

$$S = \frac{\text{moles } H_2 - \text{moles } CO_2}{\text{moles } CO + \text{ moles } CO_2} \quad \textbf{(1)}$$

$$R = \frac{H_2}{2 \times CO + 3 \times CO_2} \quad \textbf{(2)}$$

Where S is stoichiometric number and R is syngas ratio.

For methanol synthesis, the suitable syngas ratio should be around one and stoichiometric number equals to or slightly over two. In cases where the syngas ratio or stoichiometric number go over one and two, respectively, this indicates hydrogen surplus (or carbon deficiency). On the other hand, if the syngas ratio falls below 1 and stoichiometric number is under 2, excess CO and/or CO_2 is present in the feed stream.

In this study steam reforming is chosen to work at an elevated temperature and high steam to carbon ratio (S/C) when excess hydrogen is needed to achieve the specified syngas and stoichiometric ratios. However, it is important to note that varying the temperature and the amount of steam that is fed to the reformer can lead to WGS or RWGS reactions to occur, thus altering syngas ratios. For partial oxidation, the reformer herein is chosen to work as an adiabatic reformer and at elevated pressure. The generation of H_2 and CO is favored at higher temperatures, and since this reformer works adiabatically the temperature was adjusted through adjusting O_2 that is being fed to the reactor, oxygen to methane ratio being below 1 in all the proposed cases, in order to produce the required syngas ratio. In cases where DRM is involved the ratio of CO2 to methane tends to be around one, the syngas ratio and stoichiometric number is controlled through adjusting the amount of methane that is sent to DRM. For combined reforming, the ratio of syngas produced in this type reformers follows the same behavior specified by Noureldin et al. (11), where O_2 goes to a complete conversion and it reduces the syngas ratio while providing energy, where steam enhances H_2 and therefore enhancing syngas quality, while dry reforming produces more CO. The last two reforming types require energy input. All of these considerations are taken into account when simulating case 7. Challiwala et al. (12) also conducted a study on combined reforming, showing that energy requirement is lowered by the addition of O_2, and syngas quality is enhanced by the addition of steam. Since the combined reforming works under adiabatic conditions some modifications are imposed as a result of this constraint.

3.1.2.1 Steam Reforming of Methane (SRM)

Steam reforming (R-1) is the most conventional route among the other options, whereas natural gas is preheated by the flue gas from the fired heater prior to entering the reformer and react with steam.

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad \Delta H_{298K}=49.1\ \text{kcal mol}^{-1} \qquad \textbf{(R-1)}$$

The temperature of the stream exiting a steam reformer is tyoically in the range of 750 to 1050 ^{o}C, with a S/C of 2.7 (25) to avoid coke formation, and to satisfy the massive energy requirement of the reformer, a portion of methane is parted and used as a fuel for the fired heater. The operating pressure ranges from 1-20 atm (5). SMR produces a syngas that has a ratio of 3:1 hydrogen to carbon, to lower the syngas ratio, a stream of CO_2 can be injected to convert the excess hydrogen to CO through Reverse Water Gas Shift Reaction or RWGS:

$$CO_2 + H_2 \longrightarrow CO + H_2O \qquad \Delta H_{298K}=9.8\ \text{kcal mol}^{-1} \qquad \textbf{(R-2)}$$

The reformer effluent is then sent to a CO_2 removal unit where CO_2 is being separated and recycled back to the reformer with the presence of an auxiliary CO_2 source to make up for CO_2 losses.

3.1.2.2 Partial Oxidation of Methane (POx)

This option provides a ratio that is slightly lower than 2:1 hydrogen to carbon (R-3). After pre-treating the natural/shale gas, the stream is then sent to the reformer along with a pure oxygen to react and produce syngas and heat:

$$CH_4 + 0.5\ O_2 \longrightarrow CO + 2H_2 \qquad \Delta H_{298K}=-8.6\ \text{kcal mol}^{-1} \qquad \textbf{(R-3)}$$

Depending on the operational conditions and due to the abundance of O_2 in the system, CO and H_2 can be oxidized to form undesired products (26):

$$H_2 + 0.5\ O_2 \longrightarrow H_2O \qquad \Delta H_{298K}=-57.7\ \text{kcal mol}^{-1} \qquad \textbf{(R-4)}$$

$$CO + 0.5\ O_2 \longrightarrow CO_2 \qquad \Delta H_{298K}=-67.6\ \text{kcal mol}^{-1} \qquad \textbf{(R-5)}$$

The reformer operates at a high temperature and pressure 1200°C and >50 atm, respectively (5, 27, 28), therefore a further compression of syngas for the methanol converter is not required. The heat generated from this reaction could be recovered to generate steam.

3.1.2.3 Auto-Thermal Reforming (ATR)

A combination of steam reforming (R-1) and partial oxidation of methane (R-3), this reforming option doesn't require nor produce excess heat. These reactions can be carried-out simultaneously in one reactor or in separate reactors (a primary and a secondary reactor). The syngas ratio varies and can be adjusted by adjusting the load on each reactor. This type of reformers can produce just the suitable syngas quality for methanol synthesis.

3.1.2.4 Dry Reforming of Methane (DRM)

This reformer utilizes CO_2 as a feedstock and follow the chemical reaction (R-6):

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \quad \Delta H_{298K}=247 \text{ kcal mol}^{-1} \qquad \textbf{(R-6)}$$

R-6 is a highly endothermic reaction, a fired heater is required to maintain the high temperature of the reformer. Syngas ratio obtained from DRM reaction is close to unity, a further syngas condition is required to achieve the desirable ratio of 2:1 hydrogen to carbon to synthesize methanol.

3.1.2.5 Combined Reforming of Methane (CRM)

This type of reforming utilizes R-1, R-3 and R-6. Based on the objectives and the requirements of the process, reactor configuration can be modified to carry out the reactions. One possible configuration could be coupling steam reforming in parallel with dry reforming and no partial oxidation (29). The produced syngas ratio varies, and it depends on the feed composition ratios. A number of studies have revealed the potential of CRM in utilizing up to 90% of total CO_2 fed to the reformer and a net CO_2 reduction of up to 67% (14, 17, 29), and reducing the overall heating requirements of the reforming section (12). Table 2 summarizes the aforementioned reforming technologies:

Table 2 Summary of reforming technologies in order to produce syngas

Reformer Type	Reaction set	ΔH	Syngas ratio (Hydrogen-to-Carbon)
Steam Reforming	R-1	Endothermic	2.8-3.0
Partial Oxidation	R-2	Exothermic	Below 2
Dry Reforming	R-3	Endothermic	1.0
Auto-thermal Reforming	R-1 and R-2	~0	Varies, can be adjusted to 2.0
Combined Reforming	R-1, R-2 and R-3	Endothermic	Varies, can be adjusted to 2.0

3.1.3 Methanol Synthesis Technologies (4, 5, 25, 30-33)

For methanol synthesis from natural/shale gas, there is a number of different technologies that have been already established and commercialized such as Lurgi Low Pressure (LLP) methanol synthesis, Imperial Chemical Industry-Low Pressure (ICI-LP) methanol synthesis and Mitsubishi Gas Company (MGC) technology. All the aforementioned technologies have the same process train sequence, starting from natural/shale gas desulfurization, followed by reforming of methane, to methanol synthesis and finally methanol distillation or purification.

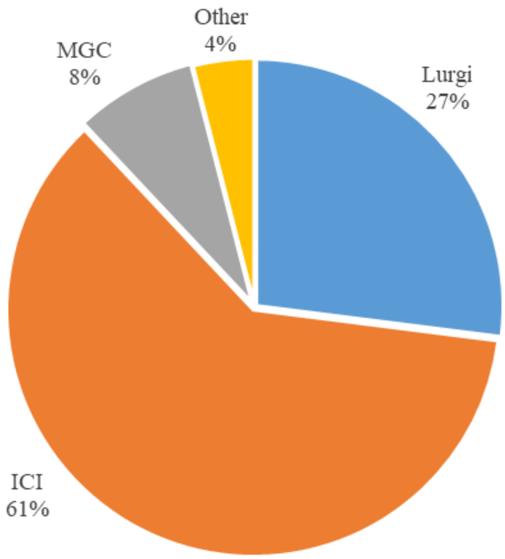


Figure 3 Global methanol Production by Technology (Reprinted from ICI, now J. Matthey)

Although, these technologies may or may not use the same reforming route and purification technology, the main difference arises in the methanol synthesis block. Each company has its own reactor design, operating conditions and synthesis loop to fresh recycle ratio (synloop) at which the methanol is produced, however, all the technologies utilizes copper based catalyst. These three technologies combined represent about 96% of methanol global capacity in today's world. The characteristics of each technology are discussed in the following sections.

3.1.3.1 Imperial Chemical Industries (ICI)

In 1966, ICI introduced the new concept of low pressure methanol synthesis by developing Cu-oxide catalyst, which also decreased the required reactor temperature. This leap reduced the cost of methanol production, given that lower pressure rated equipment and energy is needed for the process. The process used steam reforming (800-850oC) to produce syngas, and since the hydrogen carbon ratio of steam reforming is higher than 2, a syngas conditioning shift was used to adjust the ratio to around 2. The excess heat of the conditioned syngas was recovered by a steam, which was used to power the compressor in order to compress the conditioned syngas as well as the feed for the reformer. Once the conditioned syngas was compressed, it is then combined with synloop and sent to a quench reactor to be converted into methanol. The ratio of fresh syngas to synloop was typically1 to 5. The feed entered the quench reactor from the top and the pressure temperature of the reactor were between 50-100 atm and 250-300^{o}C, respectively. The converter consisted of a multiple beds and operated adiabatically, as the reaction carried out in the reactor it was quenched several times by a quench gas to maintain the reactor temperature. The heat of this reaction was recovered at the bottom of the reactor. After that, crude methanol and water were condensed from other gaseous which were partially purged and the rest were sent back to synloop. In a more sophisticated design, CO_2 would be fed directly to the steam reformer, it is true that only a fraction of CO_2 reacted to form syngas, however, this technique did not require syngas conditioning step. The exiting syngas from the latter design would go under amine absorption process where CO_2 is captured and recycled back to the reformer. An auxiliary CO_2 source is present to make-up for the lost CO_2.

3.1.3.2 Lurgi Low Pressure (LLP)

The next technology that produces methanol from natural gas is LLP. In this process, the natural gas which contains higher hydrocarbon components undergoes a pre-reformer where the higher hydrocarbon are converted to methane prior to entering the primary reformer which his basically an auto-thermal reformer. The pre-refomer is typically operated in lower temperature ranges than that of the primary reformer. Once the stream is mostly methane, it combined with steam before entering the auto-thermal reformer, whereas an oxygen is being fed as well. The autothermal reforming operates in a temperature range of 100-1400^{o}C, and a pressure up to 80 bar. The produced syngas ratio is adequate for methanol synthesis. Since the auto-thermal reformer operates in a relatively high pressure, there is no need to compress the syngas prior to entering methanol converter. The Lurgi's isothermal reactor has and internal design of shell and tube, such that the catalyst is loaded and the reaction is carried out in the tube side, while steam is fed to shell side to recover the heat from the exothermic reaction. The reactor effluent is then condensed to recover crude methanol and water and sent to the purification section to produce the desired grade of product methanol. While the other gaseous are partially purged, and the rest are compressed and recycled back to the converter. The fresh feed to synloop ratio is 1 to 5 which is almost similar to that in ICI synloop. In a more recent advancement, Lurgi announced its MegaMethanol TM technology where Lurgi claims that it has a significant cost reduction and improved process efficiency by doubling the capacity of methanol production and by introducing the dual methanol reactors.

3.1.3.3 Mitsubishi Gas Company Technology (MGC)

The Mitsubishi technology to produce methanol from hydrocarbon is almost similar in the reforming part as the other aforementioned technologies. The raw gas entering the process is desulfurized prior to the reforming step. MGC technology utilizes a steam reformer to produce syngas at 850oC, the required heat is being supplied to the reformer through natural gas as well as through excess hydrogen from methanol converter and synloop. Once, the syngas exits the reformer a heat recovery unit is installed to cool down the syngas temperature before compressing it for the methanol converter. The compressed gas is mixed with the recycled gas from the synloop before it is being fed to the reactor. The methanol reactor is a double bed quench-type reactor and utilizes a copper based catalyst. This reactor design includes a heat recovery step in an intermediate stages to capture the reaction heat. The effluent stream from the reactor is condensed to separate crude methanol from other gasses. The latter goes partially under purging to prevent accumulation of inerts in synloop. Once crude methanol is separated, it is sent to a distillation column to obtain the desired methanol grade. Depending on the feedstock and process requirements, some MGC's processes employs auto-thermal reforming along with steam reforming to produce syngas.

3.2 Flowsheet simulation

In this stage of the study, a base case flowsheet that utilizes steam reforming is developed using data from the literature. Once the simulation is performed, the inputs and outputs of the process are compared to the literature in order to validate the simulation. Each produced process scenario is modified and developed independently using the base case flowsheet to insure consistency. The available feedstock conditions are shown in table 3.

The process sequence of all the proposed cases is kept unchanged figure 4, meaning that no extra treatment unit is added nor removed. The process starts with pretreating natural gas prior to sending the feed to a fired heater, where reactant are brought to the desired temperature of reforming. The heated natural gas is then sent to the reforming unit, where one or more reformers are present. The natural gas is then distributed to the reformers along with the required reactants (e.g. steam, oxygen, etc…).

The produced syngas is then combined and cooled, where excess water is removed. An intercooled compression stage is implemented to compress syngas to the desired pressure. The compressed syngas is mixed with unreacted/recycled syngas from methanol reactor. The mixed feed is fed to the reactor where methanol is formed. Reactor effluent is expanded to allow for crude methanol recovery using a flash column. A fraction of the unreacted gaseous is purged and the rest is compressed using an intercooled compression stage prior to mixing it with the fresh feed. Crude methanol containing high concentration of water and impurities is sent to a distillation column, where a high purity (99.0wt%) methanol is obtained.

Table 3 Feedstock conditions

Raw Material	T (°F)	P (psia)
Shale gas	85	20
Steam	520	230
Oxygen	138	435
CO_2	120	310
Air	77	14.7

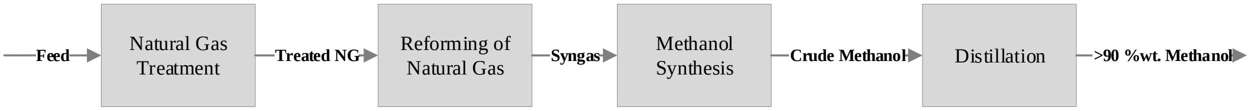


Figure 4 Natural gas to methanol process sequance

3.2.1 Feed pretreatment

The feed of natural/shale gas is assumed to be preprocessed in a nearby facility before it is sent to the methanol plant. The preprocessing step involves acid gas removal, in order to prepare the feed for the pretreatment of a methanol production. The pretreatment section of methanol plant is shown in the figure 5. The first step in the pretreatment section is to saturate natural gas before it enters the first heat exchanger, where the temperature is raised to 720 F.

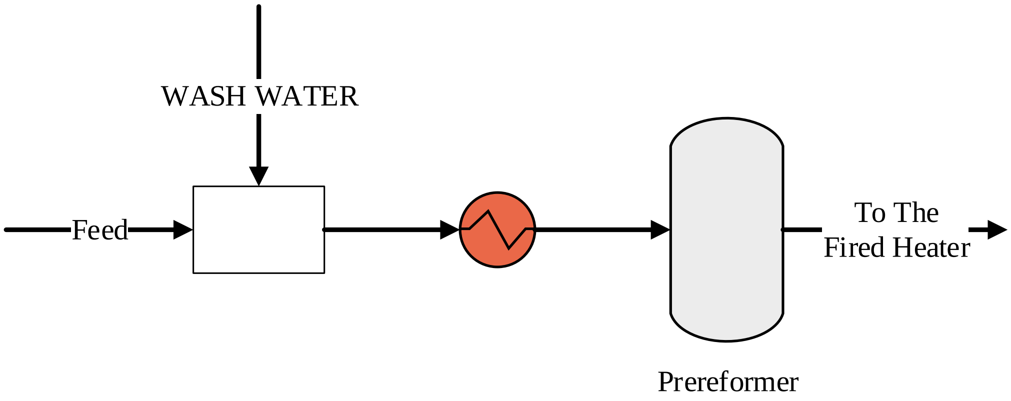


Figure 5 Feed pretreatment unit

The performer operates adiabatically and cracks down C_{2+} to hydrogen and CO in order to prevent the formation of coke when the feed is sent to the primary reformer at an elevated temperature (34). A stoichiometric (or a converter) block is used to model the pre-reformer and assuming 100% conversion of C_{2+} and heavy hydrocarbons to syngas. The ratio of steam to carbon that is fed to the reactor is based on the following chemical reaction (34):

$$C_nH_{2n+2} + nH_2O \longrightarrow nCO + (2n+1)H_2 \qquad \textbf{(R-7)}$$

For most cases, the pre-reformed feed is sent to a fired heater in order to heat the prior to reforming. In some cases, especially when a reformer operates at a relatively high pressure (e.g. partial oxidation), the pre-reformed feed undergoes a multistage compression with an intercooler in between before bringing the feed to the desired inlet temperature of the reactor. Fired heater operates at an efficiency of 75%, and it uses natural gas as fuel. Air supplied to the reactor is compressed to 20 psia and heated to 350 F to increase and maintain the efficiency of the fired heater. The fuel and air flow to the heater is adjusted using the “adjust” tool by HYSYS, in order to maintain the temperature of the hot stream at 1300 F. When heat integration is performed, heat from flue gas is recovered through cooling the flue gas (hot stream) to 250 F.

3.2.2 Syngas production

The syngas production section is the part that this study is most concerned with. The feed coming from the pre-treatment section is divided and distributed to different reformers with certain ratios based on the on the configuration. Seven designs are produced and investigated herein, and in order to have a fair comparison and assessment between all the configurations, some constraints are implemented for simulation parameters, these constrains are shown in the following table.

Table 4 Constraints imposed on the reforming block of the simulation

Reforming Section	Constraints
All reforming scenarios	Configurations must include a form of CO_2 utilization (CO_2 being fed as a reactant). Syngas ratio: $0.9<R<1.1$. Stoichiometric number: $1.8<SN<2.2$
Steam Reforming	Inlet T: 1300 F, outlet T: 1600 F. Pressure: 20 psia
	Additional heat is supplied through an external source
Partial Oxidation	Inlet T: 700 F, outlet T: ~2000 F. Pressure: 310 psia
	Adiabatic
Dry Reforming	Inlet T: 1300 F, outlet T: 1600 F. Pressure: 20 psia.
	Additional heat is supplied through an external source
WGS	Inlet T: 480, outlet T:450 . Pressure: 20 psia
Autothermal Reforming	Inlet T: 1450 F Outlet T:~2000 F. Pressure: 310 psia
	Adiabatic
Combined Reforming	Inlet T:2200 F, outlet T: ~1600 F. Pressure: 310 psia
	Adiabatic

All reformers are modeled using Gibbs block (12, 14, 16), where the equilibrium compositions are calculated through the minimization of the total Gibbs free energy:

$$\boldsymbol{G^t = \sum_{i=1}^{N} n_i G_i^o + RT \sum_{i=1}^{N} n_i ln \frac{f_i}{f_i^o}} \qquad \textbf{(3)}$$

Other fluids packages can be used including Peng-Robinson-Boston-Mathias (PRBM) which showed no significant differences in syngas production when compared to PR as reported by Zhang et al. (17), and Peng-Robinson-Stryjek-Vera (35, 36) which accounts and predicts the non-ideality of the system in methanol synthesis (37). However, when the water-gas-shift reactor is used, an equilibrium block is used with the following expression (34):

$$\boldsymbol{K_{WGS} = exp[(4578/T) - 4.33]} \qquad \textbf{(4)}$$

It is assumed that there is no pressure drop in heat exchangers across the process. Also, all compressor have a compression ratio no larger than 4. The designs and specifications of the seven reforming pathways are shown in great details in the following section, and it is worth mentioning that all co-reactants to methane ratios shown here are in molar basis, unless otherwise specified.

3.2.2.1 Case I

This scenario utilizes steam and dry reforming technologies for the production of syngas. Two possible configurations could be obtained from this combination which are shown figure 6 and figure 7. The load assigned to each reforming in both configurations is the same. In configuration 1a, the ratio of methane entering steam reformer to methane entering dry reformer is 0.6:0.4, meaning that the steam reformer is assigned for the 60% of the load in reforming section, while dry reforming has the rest of 40%. In configuration 1b, a slight modification is added, where the two reforming technologies are combined into one reactor, however, the flowrates of steam and CO_2 fed to the reactor stays same as in 1a. Thus the same load distribution applies here, where 60% of reforming is done by steam reforming and the rest is by dry reforming. The ratio co-reactants (steam and CO_2, in this case) are adjusted until the syngas ratio and stoichiometric number are met, and the ratio of steam to methane and CO_2 to methane are 2:1 and 1:1, respectively.

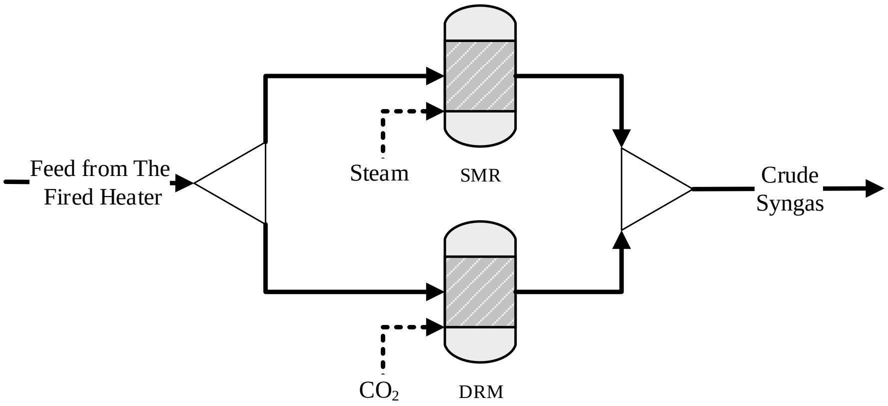


Figure 6 Case 1a

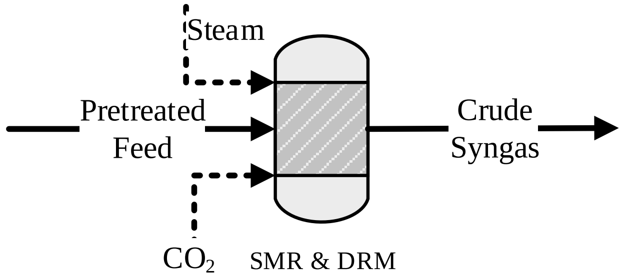


Figure 7 Case 1b

3.2.2.2 Case II

Three reforming technologies are utilized in this case, and two configurations are obtained. The first configuration implements a partial oxidation reformer in parallel to dry reforming that is in series with steam reforming as shown in figure 8. The second option combines dry and steam reforming in one reactor, while leaving partial oxidation parallel.

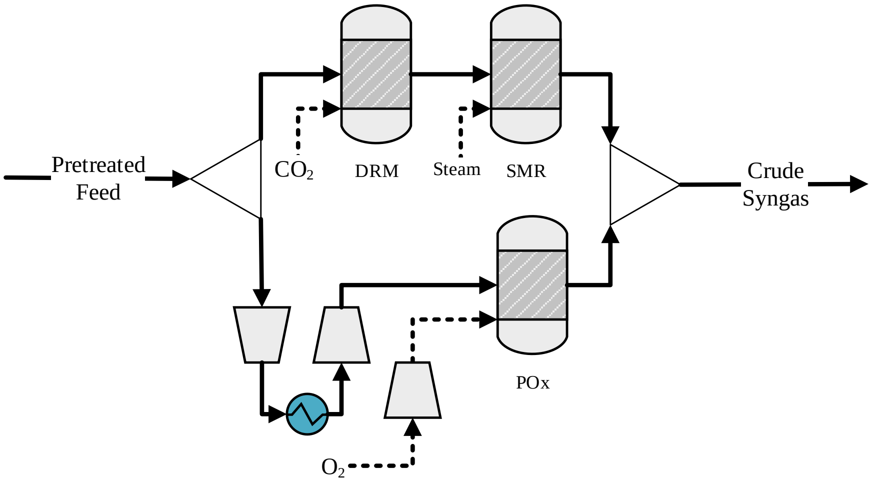


Figure 8 Case 2a

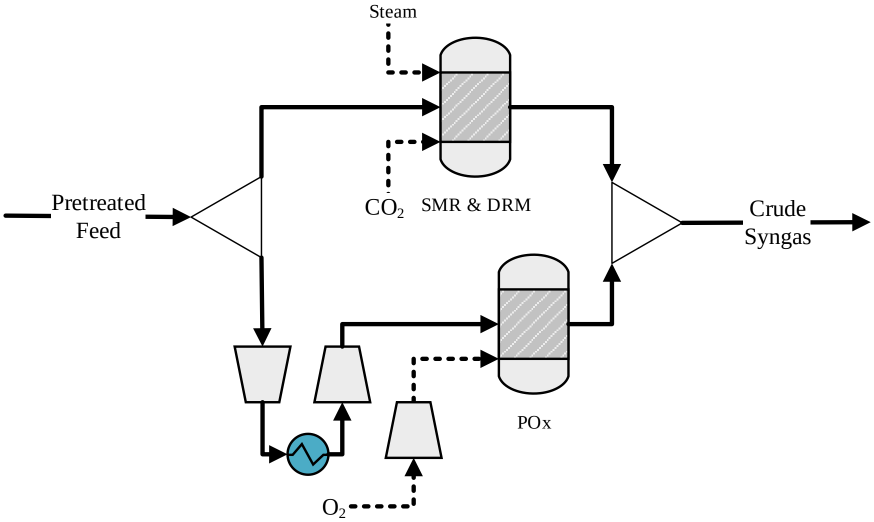


Figure 9 Case 2b

When the pre-treated natural gas leaves the pre-reformer it is split into half. The first half is sent to the fired heater and then enters dry reformer in case 2a, or the combination of dry steam reformer and steam reformer in case 2b. The other half is compressed using a multistage compression with an intercooler in between. Once the feed is compressed its temperature increases to the desired temperature of partial oxidation reformer. Co-reactants ratio to methane is the same for both configurations, where steam-to-methane is 1:1, oxygen-to-methane is 0.6:1, and CO_2-to-methane is 0.4:1.

3.2.2.3 Case III

This scenario implements three reforming technologies is parallel to each other, as shown in figure 10. 83% of the pre-reformed gas is fed to the fired heater, where 58% percent of it is sent steam reforming and the remaining 42% to dry reforming. The unused pre-reformed gas is compressed prior to feeding it partial oxidation.

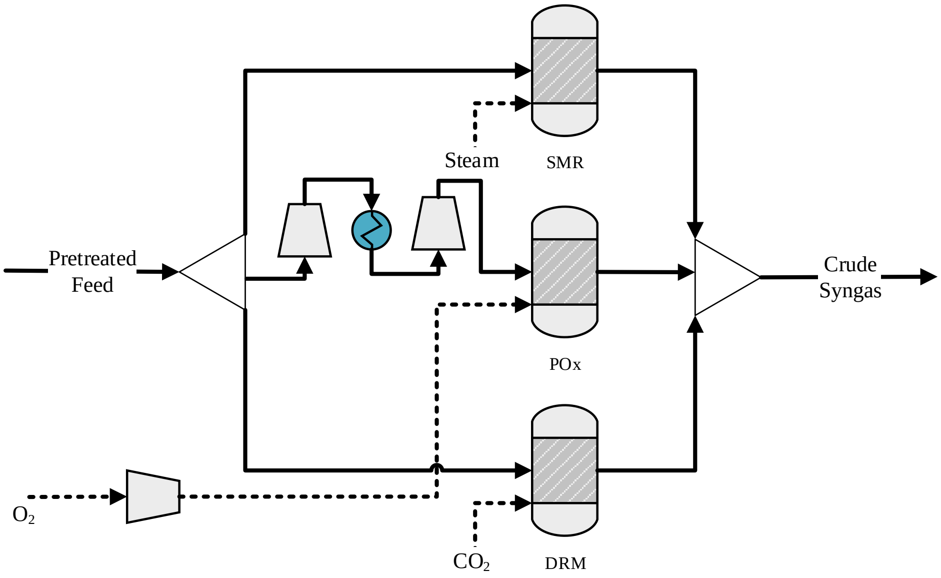


Figure 10 Case 3

Co-reactatns to methane ratios in this scenario are 2.5:1 steam-to-methane, 0.7:1 oxygen-to-methane, and 1:1 CO_2-to-methane.

3.2.2.4 Case IV

The reforming configuration in Case 4 is shown in figure 11. Heated natural gas from the fired heater is divided into two streams, the first feed stream which is three quarters of heated natural gas from the furnace goes to steam reforming, and steam-to-methane ratio that is fed to the reformer is 0.6:1. This ratio is significantly lower than any of the scenario mentioned earlier, this is due to dividing the reforming load of this stream between steam reforming and partial oxidation. Around 60% is reformed by steam reforming and the remaining is done by the subsequent partial oxidation reformer. A cooler is installed just after steam reforming in order to cool down the feed before the multistage compression. The rest of heated methane exiting the furnace is sent to dry reforming with a ratio of 1:1 carbon-to-methane ratio.

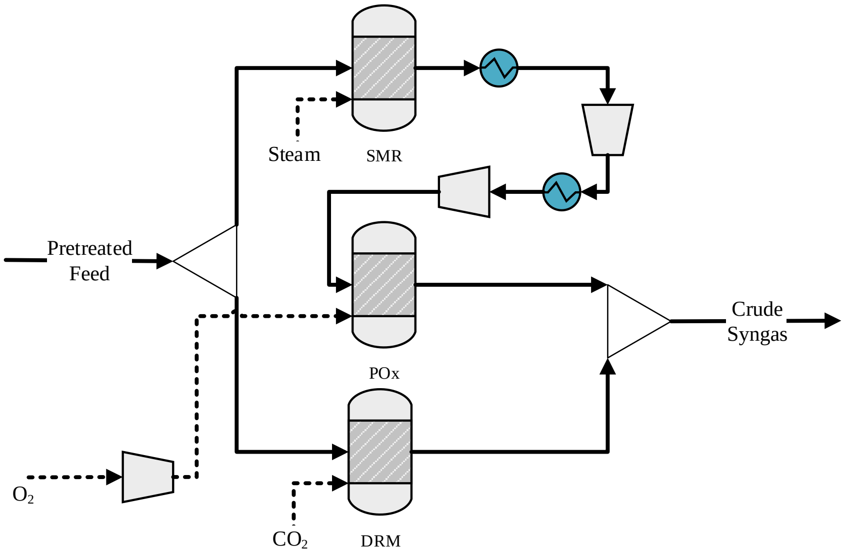


Figure 11 Case 4

3.2.2.5 Case V

This reforming configuration is similar to the one of case IV with a minor modification. A water gas shift reactor is installed after dry reforming, although case IV is able to achieve the requirements of syngas that are specified earlier, water gas shift is able to enhance syngas ratio R but not the stoichiometric number. The flowsheet of this scenarios is shown in the following figure.

3.2.2.6 Case VI

Autothermal reforming is implemented in parallel with dry reforming. Steam and oxygen are being fed to the autothermal reformer with the same ratio of 0.55:1 for both steam-to-methane and oxygen-to-methane ratios. The portion of Natural gas leaving pre-treatment section to the autothermal reforming is compressed through a multistage compression and then heated using heat exchanger. The load of autothermal reforming in this configuration is 90%, while the rest is done by dry reforming. CO_2-to-methane ratio is set to 0.75:1 in order to satisfy the constraints of syngas quality. The flowsheet of this reforming combination is shown in figure 13.

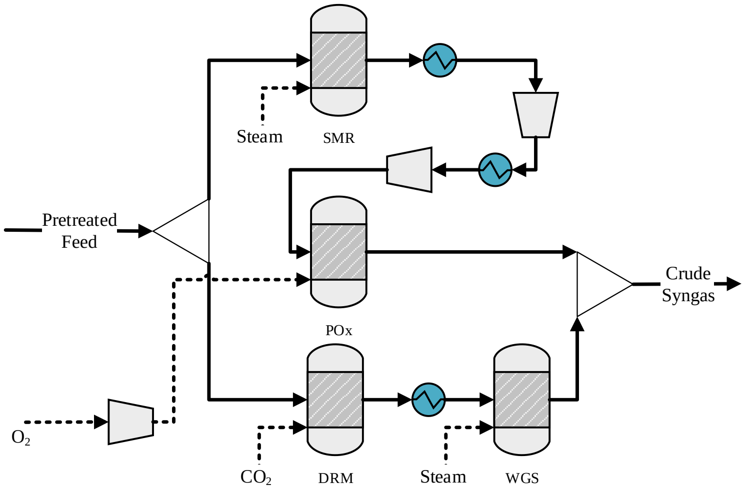


Figure 12 Case 5

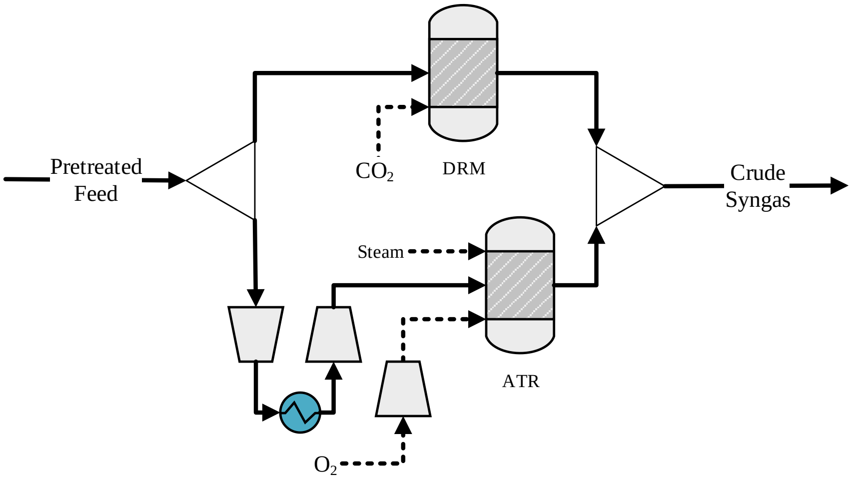


Figure 13 Case 6

3.2.2.7 Case VII

This scenario incorporates one reactor only and that is combined reforming, where all co-reactants are fed to one reactor. This the only case where the compressed methane goes through the furnace instead of entering the reformer. The ratio of reactants to methane are adjusted until the syngas ratio and stoichiometric number fall in the specified range. The ratios are found to be as follows, 1.2:1 steam-to-methane, 0.36:1 oxygen-to-methane and 0.1:1 CO2-to-methane. The configuration of this case is shown in figure 14.

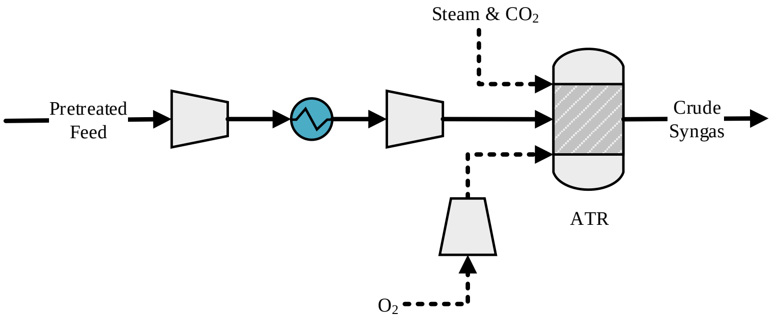


Figure 14 Case 7

3.2.3 Syngas conditioning

Once syngas is produces through various reforming pathways, the products of all reformers are combined into one stream for further condition, where water is separated from crude syngas and to prepare syngas for methanol synthesis. Since all reforming technologies operate at an elevated temperature, the combined crude syngas is cooled down in two stages. The first heat exchanger cools down crude syngas to 900 F and the second heat exchanger reduces the temperature further to 90 F, this step allows excess water in crude syngas to condense. Following heat exchangers, a flash column is installed to separate water from syngas. The recovered water requires further treatment in order to be recycled back to the process.

3.2.4 Methanol synthesis, synloop and purification unit

At this stage, syngas now has low water contents and it is ready to enter the multistage compression with intercoolers in between. Fresh syngas is compressed from 20 psia to 1100 psia. Unreacted gases leaving the synthesis flash column are compressed using a multistage compression with an intercooler in between as well. After the final compression stage, both fresh and recycled streams are cooled down to 400 F before they are mixed and fed to the methanol converter. A stoichiometric block is chosen to model the reactor with the conversion rates (38) shown in table 5. The pressurized reactor products are sent to a two stage expanders in order to recover crude methanol from unreacted and undesired gases, where the stream is depressurized from 1050 to 80 psia. As an expansion result, the temperature of the stream drops from 428 F to 120 F, however, this temperature is not sufficient to condense high quantities of crude methanol. Therefore, a cooler is installed to bring the temperature down to 90 prior to entering the flash column. The overhead products are partially purged and the remaining is compressed and recycled back to the methanol converter.

Table 5 Reactions and conversion rates for the methanol converter

Chemical reaction	Conversion rate %
Carbon monoxide hydrogenation: $CO + 2H_2 \rightarrow CH_3OH$	9
Carbon dioxide hydrogenation: $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	5
Reverse Water Gas Shift: $CO_2 + H_2 \rightarrow CO + H_2O$	3

The bottoms product is sent for purification unit. The fluid package for the distillation column is changed NRTL thermodynamic package. A distillation column with 45 trays is implemented with a partial condenser to recover high methanol purity of 99.0 wt%.

3.3 Heat and power integration (H&PI)

Heat integration is performed on all the seven cases to aid both the economics and environmental indicators. All streams passing through heat exchangers and reactors are considered in this study. Grand Composite Curves for all scenarios are produced. For power integration, energy produced from expanders are used to power compressors.

3.4 Economics

A comprehensive economic evaluation and calculations of the complete process scenarios are conducted to assess the economic viability of each option. Total capital investment of the plant calculations are shown in details in this section.

3.4.1 Raw material

Natural/shale gas is the main feedstock along with the co-reactants steam, oxygen and CO_2. Natural/shale gas compositions are shown in table 3, and it assumed that it has been preprocessed, which means that the natural/shale gas has gone under acid gas removal unit prior to sending it to the methanol plant.

Table 6 Raw material costs and product sale price

Raw Material	Price per unit
Shale gas	\$3.00/kSCF
Steam (for reforming)	\$5.00/ton
Oxygen	\$100/ton
CO_2	\$50/ton
Methanol	\$600/ton

Oxygen is separated from nitrogen in an air separation unit. The cost associated with captured CO_2 is taken into account. The following table shows the prices for the raw materials: Preliminary evaluation of the viability of reactants and products prices is done through calculating the Economic Gross Potential (EGP)

EGP= ∑ Annual rate of product P*selling price of product P - ∑ Annual feed rate of reactant R* purchased price of reactant R, where …(5)

EGP > 0 process could be considered for further analysis

EGP <= 0 process is not economically viable

and the Metric for Inspecting Sales and Reactants (MISR)

MISR = (∑ Annual rate of product P*selling price of product P/∑ Annual feed rate of reactant R* purchased price of reactant R) …(6)

MISR > 1 process could be considered for further analysis

MISR <= 1 process is not economically viable

These indicators provide insights on whether one should proceed further with analyzing and developing the process based on the feedstock and products quantities and prices.

3.4.2 Total Capital Investment (TCI)

Total capital investment is the sum of Fixed Capital Investment (FCI) and Working Capital Investment (WCI), and it represents the amount of money needed to install and provide all the facility with all needed services and process equipment. FCI consists mainly from purchasing equipment and installing these equipment in the plant. The majority of equipment cost estimation is done using ASPEN Process Economic Analyzer, except for some equipment such as reactors where the literature is used to estimate the cost.

3.4.2.1 ASPEN Process Economic Analyzer (ASPEN PEA)

This powerful tool provides cost estimation of process equipment. ASPEN HYSYS has a built-in function where one can export the flowsheet, hence allowing ASPEN PEA to size and to provide a practical equipment cost based on information collected from the user's process flowsheet. In this work, ASPEN PEA is used to estimate the cost of heat exchangers, compressors, flash and distillation columns.

3.4.2.2 Cost curves for purchased equipment costs

For some equipment such as the fired heater, ASPEN PEA does not assist the user with estimating the purchased cost. Therefore, the cost of the fired heater is estimated using correlations by Towler and Sinnott (40) in the form of

$$Ce=(a + bS^{n}) * (\text{CEPCI Equipment (Jan 2018)}/ \text{CEPCI Equipment (Jan 2018)})$$

Where

Ce= purchased equipment cost on U.S. Gulf Coast basis, Jan 2010 (CEPCI Equipment=698.2)

a&b= costs constant

S= Size parameter (MW)

n= exponent for that type of equipment

For fired heater the constants are shown in the following table

Table 7 Fired heater cost constants

a	b	n	CEPCI Equipment (jan-18)
43,000	111,000	0.8	695

3.4.2.3 six tenths

Some equipment such as reactors, where they might have complex internal design and lack economic evaluation data, Sixth-Tenths-Factor Rule is used to estimate the cost of similar equipment but with different sizes:

Equipment Costb = Equipment Costa * (Size B/Size A)0.6 * (CEPCI Equipment (time of estimating equipment A cost)/ CEPCI Equipment (Jan 2018)) … (7)

The terms Equipment Cost$_a$ and Size A are found in the literature, while the term Size B can be obtained from simulation data, and in this case is the flowrate entering the reactor. Table 8 shows the basis of reactor cost estimation in this study (41, 42):

Table 8 Cost estimation parameters for reformers

Reactor	Reference capacity (kgmol/hr)	Reference cost ($)	Year	CEPCI for Equipment
ATR/POx/CRM	14,494	$ 4,710,600	2014	698.8
SNR	4050	$ 4450,00	2012	693.6
DRM	294	$ 178,800	2012	693.6

3.4.2.4 The Hand method (39)

To determine the FCI of the project, Hand method is used when all the delivered equipment costs are estimated. Hand expression calculates the FCI of plant by accounting for other types of expenses that are associated with the equipment and the plant such as piping, installation, etc. Hand factor is dependent on equipment type, table 9 provides hand factor for each equipment category.

Table 9 Hand factor for equipment

Equipment Type	Hand Factor
Compressors	2.5
Distillation columns	4.0
Fired heaters	2.0
Pressure vessels/tanks	4.0
Heat exchangers	3.5
Instruments	4.0

3.4.3 Operating costs and Utilities

It is assumed in this work that the natural/shale gas is preprocessed in a facility to remove acid gas. The cost of this treatment is calculated from using data from the literature (43), and since the feedstock is fixed for all cases, the cost of this preprocessing is estimated to be $155 MM/yr. The costs of utilities used are shown in the following table

Table 10 Costs of utilities

Utility	Price per unit
Heating	$4.00/MMBTU
Cooling	$2.00/MMBTU
Power	$0.05/kWh
Waste treatment	$0.05/ton

3.5 Profitability

The profitability of the various reforming cases are assessed through Return Of Investments (ROI). ROI is calculated through the following expression:

ROI= Annual after tax profit / (FCI+WCI) …(8)

Where:-

WCI = 15/85 * FCI

and the annual after tax profit can be calculated using:

Annual after tax profit= (Methanol sales – raw material – utilities cost – depreciation) x (1 – tax rate) + depreciation + Tax credit - carbon Tax …(9)

Tax credit is basically the amount of CO_2 that is avoided, whether that is in a direct way such as integrating CO_2 as feedstock or through applying heat and power integration where less energy is used and thus less carbon footprint.

3.6 Environmental

A comprehensive environmental assessment is thoroughly performed to determine the most sustainable scenario, by accounting for direct and indirect CO_2 emissions and waste water generation. Aside from purging and flaring, there are different sources within the process that contributes to CO2 emission indirectly. These sources are presented in table 11(44, 45)

Table 11 CO_2 emissions sources and the corresponding emission factor

Emission Source	Emission Factor (lb CO_2)
Heating	116.6 /MMBTU
Compression	292.7 /MMBTU
Natural gas production	0.270 /lb
Steam production	0.473 /lb
Oxygen production	0.273 /lb
CO_2 capturing	0.063 /lb

As it can be seen from table 11, that the cooling utility is not included as a CO_2 source since the process utilizes cooling tower where the water is cooled by ambient air. Also, this work takes into account the CO_2 being emitted due to producing reactants such as steam, oxygen and the capture of CO_2. Sustainability Weighted Return on Invest Metric (SWROIM) (39) is used to reflect the sustainability performance on the ROI. CO_2 target is set based on lowest emissions being emitted from an existing gas-to-methanol plant:

$$\boldsymbol{ASP_p = AEP_p \left[1 + \sum_{i=1}^{N_{Indicators}} w_i \left(\frac{Indicator_{p,i}}{Indicator_i^{Target}}\right)\right]} \qquad \textbf{...(10)}$$

Where

AEP_P: Annual Economic Profit, **i**: Index for sustainability indicators, **w_i**: weighing factor, **$Indicator_i^{Target}$**: Obtained from process integration benchmarking or largest value from all projects, **$Indicator_{p,i}$**: Value of the ith sustainability indicator for pth project

And the sustainability indicator for CO_2 is calculated by

$$\boldsymbol{\frac{CO_{2,base} - CO_{2,after\ PI}}{CO_{2,base} - CO_{2,best\ process}}} \qquad \textbf{...(11)}$$

Where $CO_{2,\text{ best process}}$ is taken to be equal to 1lb CO_2 / 1 lb methanol (46). Whereas the target for water is calculated based on the total discharged waste water over the actual amount of treated and recycled waste water. The weighing factors for CO_2 and waste water generation are 0.25 and 0.10, respectively.

3.7 Safety

The Dow Fire and Explosion Index (F&EI) is used to assess and rank the safety of the proposed designs. The factors for the general process hazards that are taken into consideration in this work are the nature of the reaction (e.g. exothermic or endothermic), material handling, and the number of process units. For the special process hazards, the factors are toxic material(s), operating pressure, and the quantity of flammable material used in the process. Safety analyses are performed and presented with respect to the reforming section only.

4. RESULTS AND DISCUSSION

4.1 Process Economics

4.1.1 Base Case

The simulation of several reforming configurations to produce methanol is carried out to highlight the differences in the economic profitability and sustainability of each design. Starting with the MISR and EGP defined earlier by expressions 5 and 6, all cases are showing economic potential for further analyses based on reactants and product costs. These two metrics should be only used to evaluate the economic feasibility of the process at the early stage of the work, further analyses are required to determine whether a certain project is viable or not.

Table 12 MISR and EGP values obtained all design options

Scenario	MISR	EGP
Case 1a	2.7	$ 689,760,106
Case 1b	2.9	$ 779,526,822
Case 2a	2.1	$ 499,858,742
Case 2b	2.1	$ 498,804,113
Case 3	2.4	$ 622,987,028
Case 4	2.1	$ 482,247,111
Case 5	2.1	$ 496,863,040
Case 6	1.7	$ 353,177,502
Case 7	1.4	$ 194,863,766

For the Fixed Capital Cost (FCI), figure 15 illustrates the FCI per equipment category per case. It can be seen that there is a general agreement on the cost distribution, where compressors costs more than 60% of the total FCI. Although reactors are ranked second in terms of their contribution to the FCI of each case, reactor share of the FCI tends to be around (25-30%) of FCI throughout all the cases. Heat exchangers (including fired heater, rebuilder and condenser) and columns (including both distillation and flash columns) represent less than 10% of total FCI.

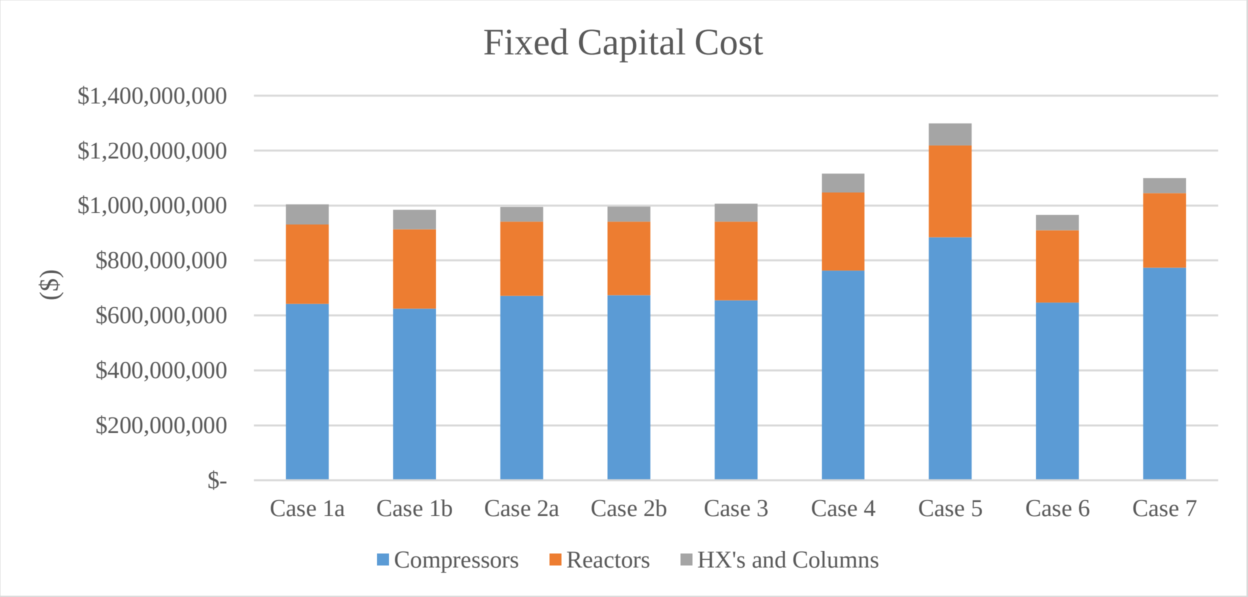


Figure 15 Breakdown for the FCI by equipment type

For compressors, the small in difference compressors costs between case 1 (a&b) and case 2 (a&b) is due to the addition of a partial oxidation reactor in the latter cases, where it operates in an elevated pressure. Although the configuration in case 5 is slightly different than the configuration in case 4, there is a distinct increase in the share of compressors in case 5. This is because the load placed on steam reforming (operating in series with partial oxidation in both cases 4 and 5) is significantly larger in case 5 rather than 4, thus reactor effluent passing through the multi stage compressors in case 5 is larger in terms of the flowrate and therefore requires larger compressors. For cases 6 and 7, where the first has an ATR operating in parallel to a dry reforming and the latter has only one combined reforming, the noticeable increase in compressors cost is due to compressing the whole feed of natural gas in case 7 prior to feeding it to CRM. Whereas in case 6, part of the feed is diverted to dry reforming which operates under low pressure than that of ATR.

Unlike the fixed capital cost where reactors represent 10% of total FIC, utilities supplied to reactors are the largest for most cases. However, when oxygen is used as a co-reactant, the utility required by reactors for reforming of natural gas drops significantly. Since all reactor utilizing oxygen operates adiabatically, thus no heating is required. This example can be seen clearly in figure 16 where case 7 has almost no utility required for reactors, except for cooling methanol reactor.

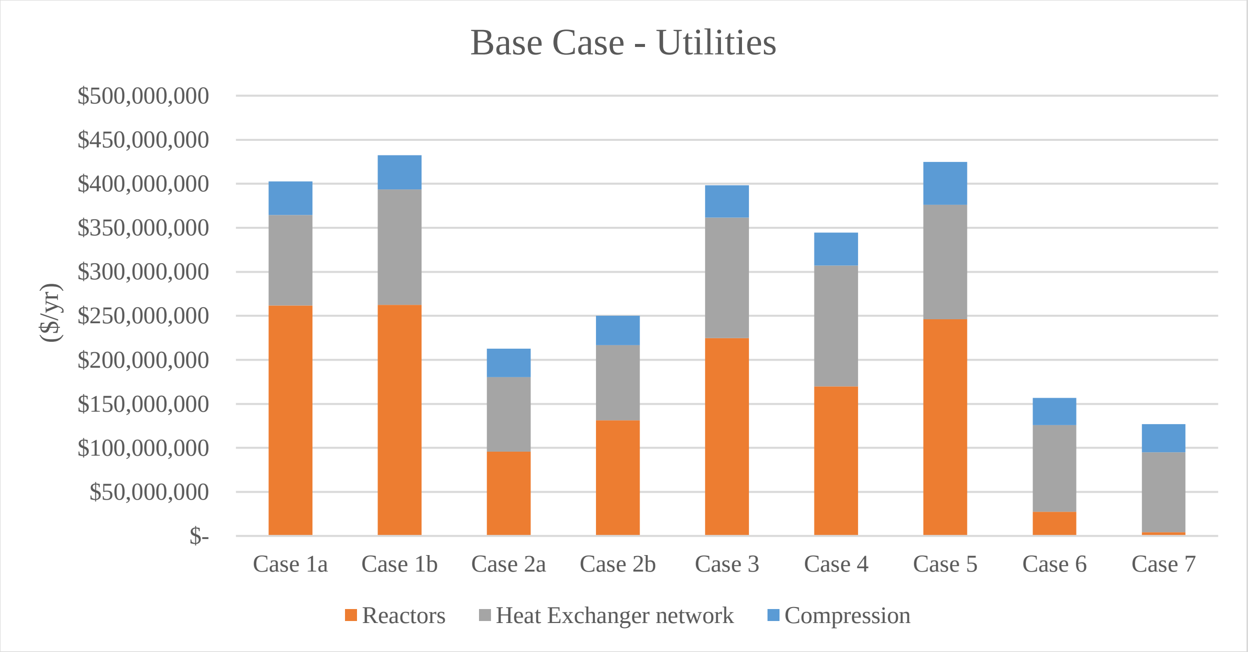


Figure 16 Utilities cost per equipment type - Base case

Figure 17 shows the ROI of the base case vs production rate of methanol. There is a general trend where the ROI increases as the plant's capacity increases. Since the production of methanol in this work depends solely on the compositions of syngas produced, the extremely low ROI in case 7 traces back to the fact that only one reactor is used to produce syngas, and since there are number of constraints, the degrees of freedom here becomes limited for this type of design, thus lowering methanol production rate. Although case 4 and 5 have more production capacity than case 6, yet they have lower ROI than case 6, owing it to implementation of more reactors in the reforming section compared to case 6. In addition, the reforming section in case 6 requires significantly lower utilities than that of case 4 and 5, since the majority of reforming load in case

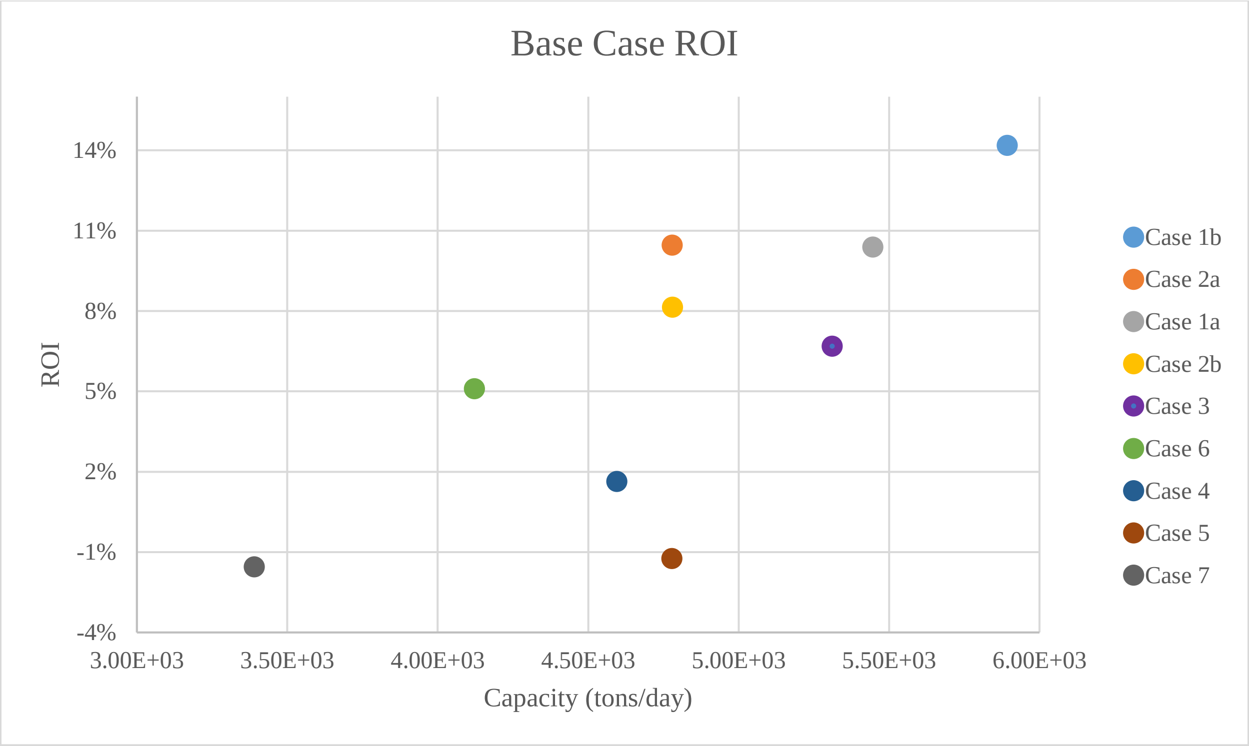


Figure 17 ROI vs production capacity for the different reforming options

6 is placed on the adiabatic ATR. The same argument can be made between the cases of 2(a,b) and case 3. It can be seen clearly that case 3 has more methanol production capacity than 2a and 2b, however, due to higher utility requirements for case 3 than utility requirements of both cases in 2 ($400 MM/yr compared to < $250 MM/yr), the ROI is slightly lower in case 3. In general, methanol production capacity plays a big role in the calculations of the ROI, as the capacity increases the profitability of the process increases as well. However, for some cases where utility requirements are significantly higher it could overcome the profit generated from methanol sales and therefore decreases the profitability of that design configuration.

4.1.2 Cases After Applying Heat and Power Integration (HP&I)

The economic performance of all the cases is enhanced by conducting heat and power integration. It is important to note that the streams entering and exiting the fired heater in this analysis are not considered except for the flue gas stream. When heat integration is implemented and Grand Composite Curves produced, nearly all process configurations required 0 heating utilities, except for cases 1a and 1b where the minimum heating utility needed are 16 and 43 MMBTU/hr Figure18. This due to not utilizing oxygen as a co-reactant, where it provides a tremendous amount of heat that can be used toward heating endothermic reactions such as steam reforming and dry reforming. Flue gas exiting the furnace is another major source of energy for replacing heating utilities, the heat from the flue gas is recovered and used to preheat reactants.

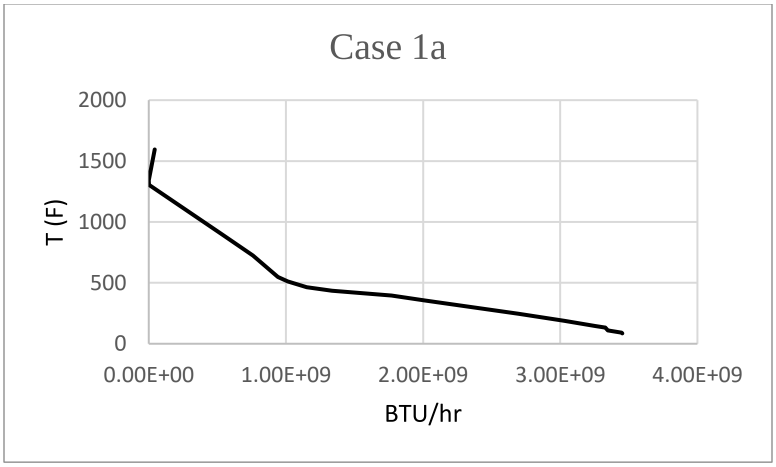


Figure 18 Case 1a grand composite curve

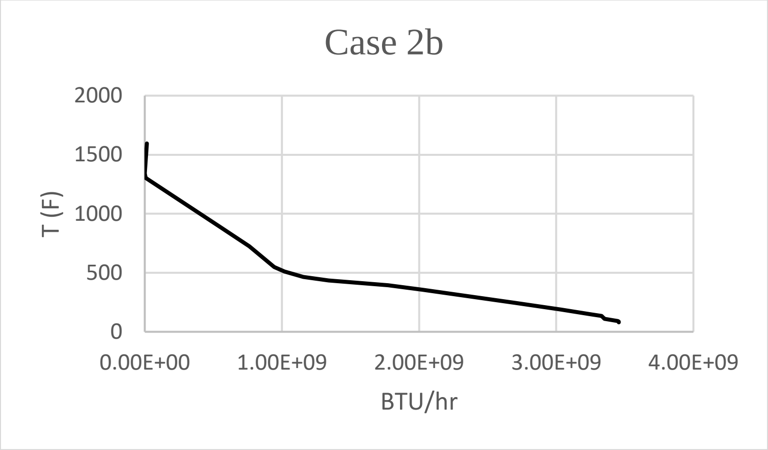


Figure 19 Case 1b grand composite curve

Other heating sources found within the process are streams exiting compressors, since there are multiple multistage compression in the process. Heat produced from methanol synthesis is used to power the compressors since minimum heating utility target is already satisfied, expanders are used as well to provide power to compressors. The following table shows the savings and improvements that resulted from heat and power integration. Almost all the scenarios are profitable when H&PI is performed, however, for configuration in case 7, the issue of an extremely low ROI stems from its low methanol capacity as indicated earlier. In contrast, cases with higher utility requirement in the base case section have expressed the highest utility savings when H&PI is performed, thus higher ROI. This jump in the ROI highlights the importance of H&PI step during process synthesis.

Table 13 ROI and Utilities cost before and after H&PI

Scenario	ROI (%)		Utilities ($)	
	Before H&PI	After H&PI	Before H&PI	After H&PI
Case 1a	10	28	402,638,329	103,485,736
Case 1b	14	27	432,256,038	105,885,634
Case 2a	10	18	212,572,344	88,455,147
Case 2b	8	18	250,237,000	92,380,773
Case 3	7	24	398,170,900	223,369,491
Case 4	2	14	344,439,555	116,759,177
Case 5	-1	16	424,783,119	58,309,628
Case 6	5	10	156,859,615	82,953,850
Case 7	-2	1	127,079,791	72,611,300

4.1.3 Sensitivity Analysis

4.1.3.1 Natural/shale Gas cost and Methanol Selling Price

A sensitivity analysis is performed to explore the effects of natural/shale gas price fluctuation and variation in methanol demand, thus the sale price. The sensitivity analysis is conducted on cases after H&PI is performed. Table 14 shows the result of this analysis, and demonstrate the feasibility of the proposed designs under varying feed cost and product selling price. As one can clearly see that Case 1a has the most economic viability among other designs, especially under low methanol selling price of (0.20 $/lb). On the other side, cases 6 and 7 are not viable when methanol prices are under 0.5$/lb and no matter what the feed cost is. This illustrate that these design configurations shall not be considered for implementation under any circumstance due to their poor ROI even at higher methanol selling prices.

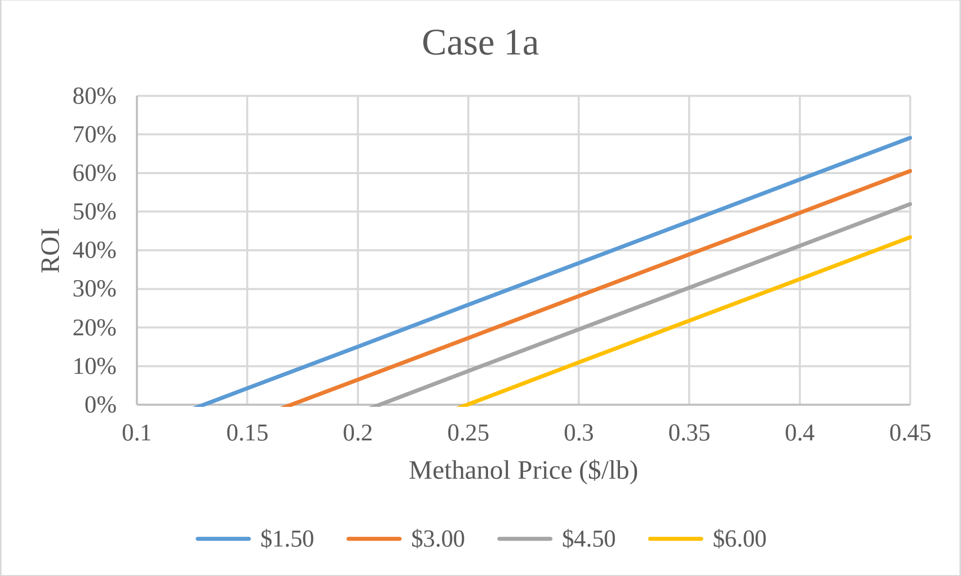


Figure 20 Sensitivity analysis for the most profitable case

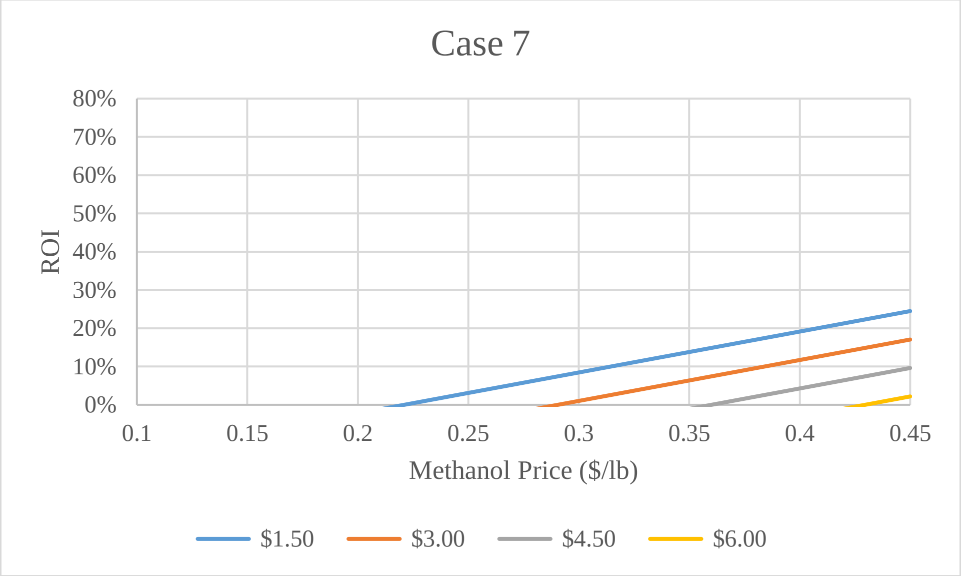


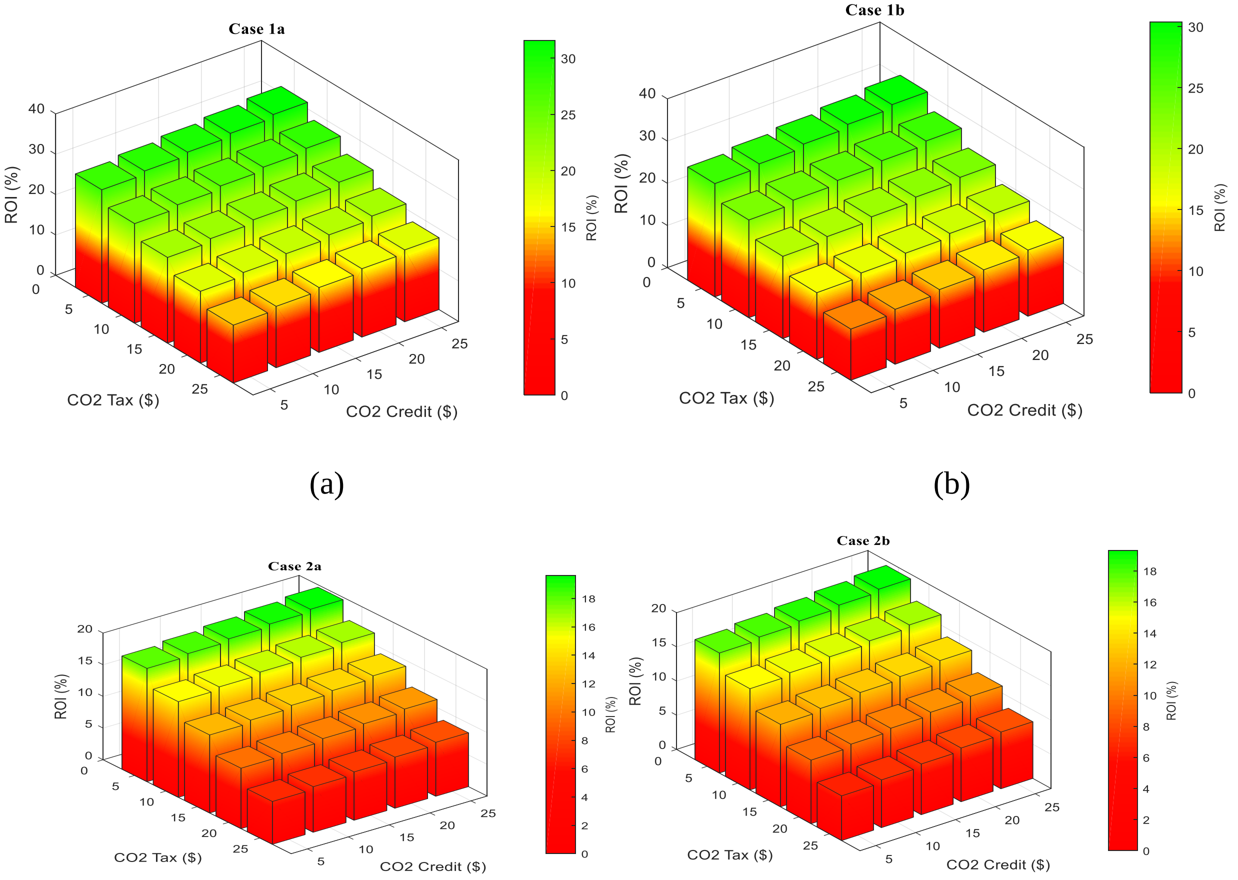
Figure 21 Sensitivity analysis for least profitable case

Table 14 Economic viability of the reforming cases at various feed and product prices

Feed Cost ($/kSCF) / Methanol selling	0.20	0.25	0.30	0.35	0.40
1.5	Case 1a	Case 1 (a&b) Case 2 (a&b) Case 3 Case 4 Case 5	Case 1 (a&b) Case 2 (a&b) Case 3 Case 5	Case 1 (a&b) Case 2 (a&b) Case 3	All cases
3.0	-	Case 1 (a&b) Case 3	Case 1 (a&b) Case 2 (a&b) Case 3 Case 5	Case 1 (a&b) Case 2 (a&b) Case 3	All cases except for 7
4.5	-	-	Case 1 (a&b) Case 3	Case 1 (a&b) Case 2 (a&b) Case 3 Case 4 Case 5	All cases except for 7
6	-	-	-	Case 1 (a&b) Case 3	Case 1 (a&b) Case 2 (a&b) Case 3 Case 4

4.1.3.2 Carbon Tax and Carbon Credit

Although this study takes into account the price of capturing CO_2, the change in profitability of a process due to carbon emission and carbon credit is evaluated. Since environmental regulations could severely affect the economic viability of a process (47). Therefore, a sensitivity analysis on carbon tax and carbon credit is conducted to further explore the limits of each proposed design. 3-D plots are generated by MATLAB to show how environmental regulations represented by carbon tax and carbon credit (which is in this study is how much carbon have been utilized as feedstock during the process of methanol production) can affect the proposed process designs. The calculations herein are based on \$3.00/kSCF for natural gas and \$0.30/lb for methanol. In general and from figures 22 and 23, one can see that the color of the 3-D bars tend to change more with changing carbon tax rate rather than the variation of carbon credit rate. This is due to the fact that more carbon is being emitted by the process rather than being consumed. However, cases such as 1a and 1b still can make profit even at higher carbon tax rate and low carbon credit. In contrast, when even a low carbon tax value (\$5/ton) is placed and a high value for carbon credit is given (\$25/ton), cases 4, 5 and 6 would be still affected negatively by the regulations and are hardly making a profit, hence becoming economically unattractive. For the other process scenarios, namely 2 (a&b) and 3, are still feasible when a carbon tax of \$5/ton is implemented and without giving any credit for CO2 utilization.



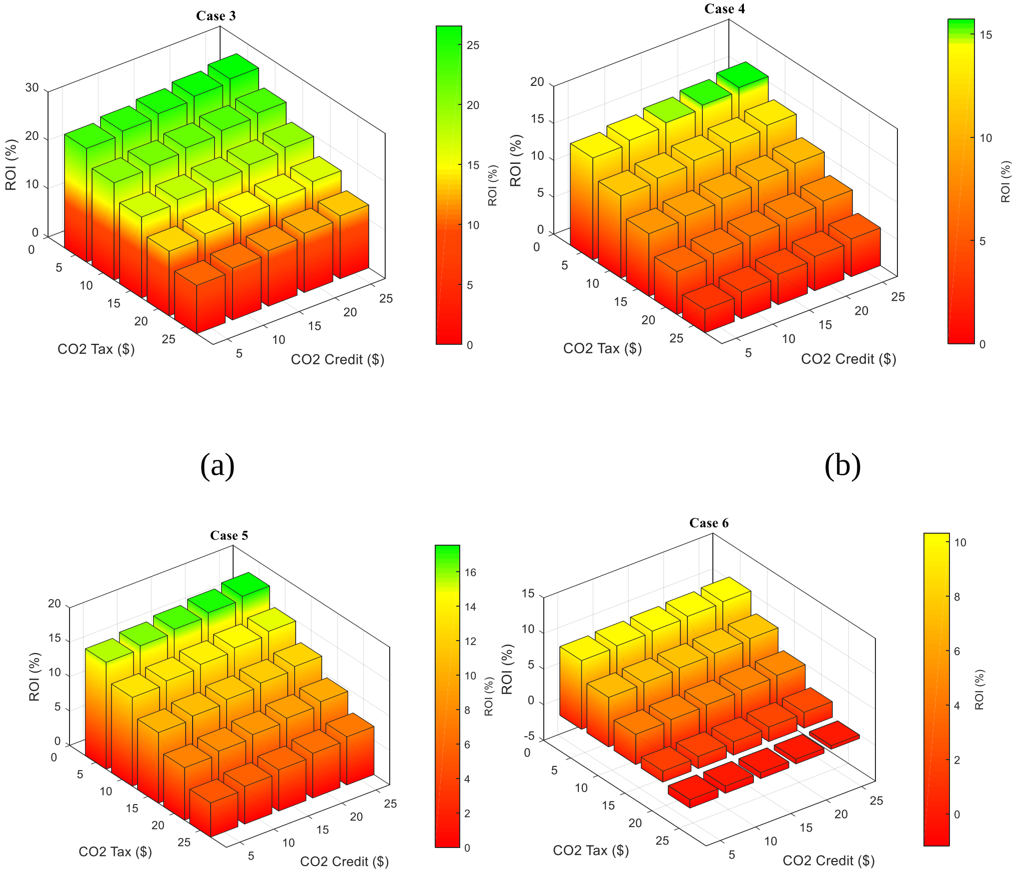
(a)

(b)

(c)

(d)

Figure 22 Sensitivity analysis for cases (a) 1a (b) 1b (c) 2a (4) 2b



(a)

(b)

(c)

(d)

Figure 23 Sensitivity analysis for cases (a) 3 (b) 4 (c) 5 (d) 6

4.2 Sustainability

The sustainability of the process is evaluated and quantified based on CO_2 emissions and waste water generation. CO_2 emission sources are calculated as explained and described earlier in the methodology section. Figure 24 shows the improvements of CO_2 emissions reduction after implementing heat and power integration.

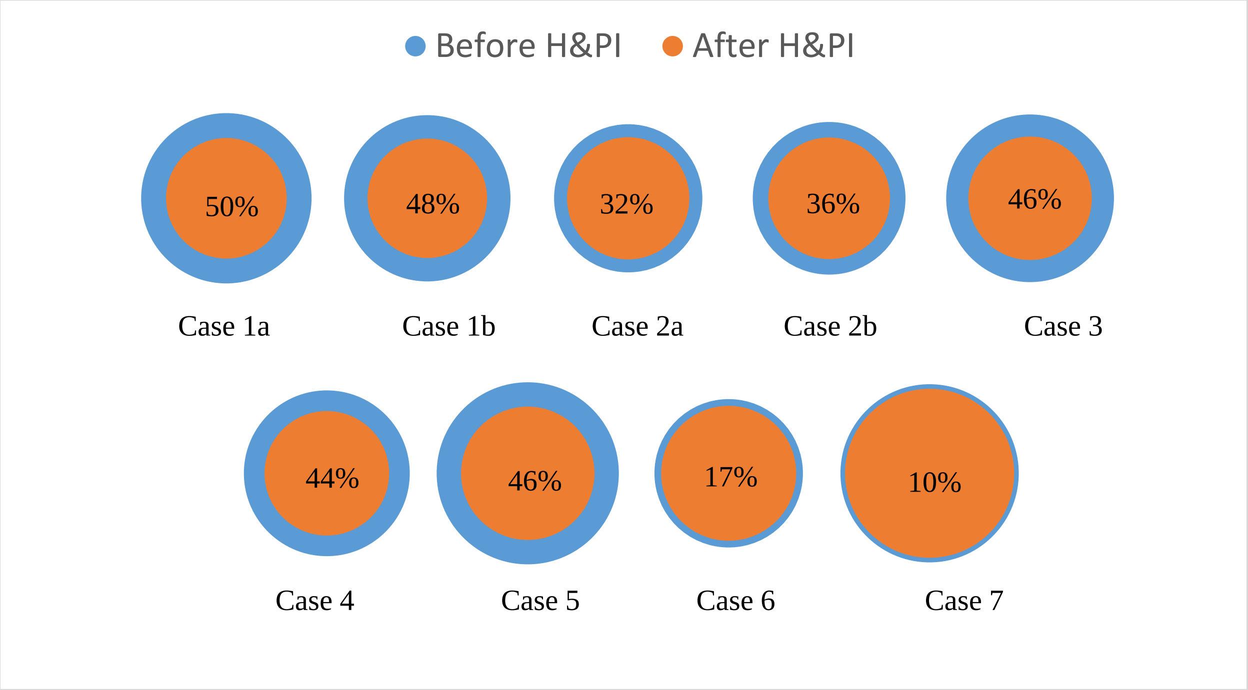


Figure 24 Relative CO_2 emissions by case

Overall, H&PI improved the sustainability of all scenarios, especially the ones with higher utility consumption before H&PI. This is the same analogy as how the ROI of all the cases has increased after performing H&PI. Although integrating CO_2 as a feedstock reduces the net CO_2 emissions, CO_2 emissions are heavily impacted by H&P. The above figure represents only how CO_2 is relatively reduced and not the magnitude of CO_2 emissions that are produced by each case. Table 15 presents the CO_2 emissions by scenario in lb CO_2/ lb MeOH

Table 15 CO_2 emissions by case after H&PI

Scenario	lb CO2 / lb MeOH
Case 1a	3.33
Case 1b	3.27
Case 2a	3.43
Case 2b	3.39
Case 3	3.49
Case 4	3.55
Case 5	4.08
Case 6	4.18
Case 7	6.55

In addition to CO_2 emissions, waste water generation is looked into to better assess the sustainability aspects of all the processes. Unlike CO_2 emissions, all scenarios are performing well in waste water utilization, where the majority of waste water being produced is treated and sent back to the process. This due to the recovery of large amounts of waste water from two sinks. The first sink, is the flash column where water is separated from crude syngas. The second sink, is the bottoms of distillation column, where water is separated from methanol to produce a high purity methanol. The remaining unrecoverable waste water is either being purged as water vapor or traces of water exiting with the 99 wt% methanol from the distillation overhead. Table 16 shows the amount of waste water that is being recovered, treated and recycled to the process per each scenario. To better quantify these results, SWROIM is used to reflect the sustainability performance of a process on its ROI. Table 17 shows the SWROI values for all the cases, where the weighing factor is chosen to be 0.25 for CO_2 emissions and 0.1 for waste water generation. It can be clearly seen that the ROI of all processes is improved, however, the rate of improvement differ from case to another, and that is due to their original ROI values and sustainability performance. For example the improvement in case 7 is insignificant when compared to case 1a or case 3. In general, the average improvement of all the cases hovers around 20% of the original ROI.

Table 16 Waste water recovered and recycled back to the process

Scenario	Waste Water Recovery %
Case 1a	98
Case 1b	97
Case 2a	94
Case 2b	97
Case 3	98
Case 4	95
Case 5	98
Case 6	98
Case 7	99

Table 17 The impact of sustainability on the ROI using SWROIM

Scenario	ROI	SWROIM
Case 1a	28%	35%
Case 1b	27%	33%
Case 2a	18%	21%
Case 2b	18%	21%
Case 3	24%	29%
Case 4	14%	17%
Case 5	16%	19%
Case 6	10%	11%
Case 7	1%	1%

4.3 Safety Analysis

The safety of each design are assessed with the aid of the Dow F&EI. The ranking of the safer reforming scenario is as follows:-

Case 1b > Case 1a > Case 7 > Case 4 > Case 6 > Case 3 > Case 5 > Case 2b > Case 2a

For cases 1a and 1b, the absence of the high pressure reactor vessel as well as the absence of the exothermic reaction (no oxygen stream) have a significant impact that improved the safety of these scenarios when compared to the other alternatives. Although case 7 utilizes oxygen as one of the co-reactants and operates under high pressure, this process scenario utilizes one reformer, hence eliminating hazards that may stem from adding another reactor. For cases 2a and 2b, the increase of the process dependence on the exothermic reaction to produce syngas has led to elevating the hazards that are associated with these scenarios.

5. CONCLUSION AND RECOMMENDATION

In conclusion, a comprehensive evaluation of the economic and environmental aspects of different configurations and combinations of reforming technologies to produce syngas that is suitable for methanol synthesis. A methanol plant that utilizes conventional reforming technology (e.g. steam reforming, partial oxidation or autothermal reforming) as the primary source for syngas is considered for modifications, where other forms of syngas production from CO_2 are incorporated within the process. The modifications are contained solely within the reforming section, while maintaining the rest of the process unchanged in order to compare the alternatives. Nine unique reforming options are produced, and ASPEN HYSYS is used to simulate the processes. ASPEN Process Economic Analyzer is utilized to size and calculate the costs of some process equipment such as heat exchangers and compressors. Values from the literature are used to evaluate the cost of reactors and turbo-expanders through Six-tenths factor rule. The FCI of all options is calculated using the Hand factor and Hand method. Heat and power integration is conducted to enhance both economic and environmental performance of the proposed design. Direct and indirect CO_2 emissions are taken into account, where direct emission is calculated by how much the process is directly emitting CO_2 into the atmosphere. While indirect CO_2 emissions are concerned with carbon footprint natural/shale gas, co-reactants, and energy production. In addition to CO_2 emissions assessment, waste water sinks are identified in order to recover and recycle waste streams. Results show that ROI increases with increasing production except for some cases such as case 5, where four reactors are implemented in the reforming section leading to a considerably higher FCI, therefore overcoming the high production of methanol and decreasing the ROI. Although when H&PI is not implemented some processes are making profit, yet when H&PI is conducted the ROI increases significantly for most cases, with case 1a (where a steam reforming is in parallel with dry reforming) being the most profitable design. In contrast, case 7 or combined reforming showed the lost ROI, due to the imposed constraints of syngas production discussed earlier and the lack of degrees of freedom when utilizing one reactor. SWROIM is used to quantify sustainability metrics and reflect them on the ROI of the process. The results showed significant ROI increase for all cases except for case 7 where no improvement where only 10% CO_2 avoidance is achieved compared to 50% avoidance achieved by case 1a. Sensitivity analysis is conducted to evaluate the fluctuations of natural/shale gas prices as well as methanol selling price. Case 1a and to less extent cases 1b and 3 showed the most robust economic profitability when the prices of methanol dropped. Also, sensitivity analysis is extended to measure the impact of regulations carbon tax and carbon credit. Analysis shows that carbon tax has higher impact on the ROI when compared to tax credit, and this is because all the processes emit more CO_2 than they consume to produce syngas. Results from economic and sustainability analyses suggest that all current conventional processes can be modified to incorporate dry reforming and make profit, except for processes that utilize autothermal and combined reforming.

5.1 Future work

The presented work can be extended to involve

- Lift constraints that are included in this study such as:
    - Reformers that utilize oxygen as a co-reactant operates adiabatically
    - Adjust the temperature to find the optimal temperature for each reactor in each proposed scenario
- Optimize reactants ratios that are being fed to the reformer, where economic and sustainability indicators are taken into account

- Reflect and provide insights on the role of catalysis and intrinsic kinetics of methanol synthesis reaction on the process, through simulating process outcomes when a catalyst with certain functions has been developed
- Use an equilibrium block to replace the stoichiometric block for methanol converter:
    - Develop a kinetic expression from the literature
    - Optimize the kinetic parameters to account for the variation in syngas ratios, especially CO and CO_2 contribution to methanol synthesis

REFERENCES

1. Liss WE. Impacts of Shale Gas Advancements on Natural Gas Utilization in the United States. Energy Technology. 2014 Dec;2(12):953-67.

2. Riaz A, Zahedi G, Klemeš JJ. A review of cleaner production methods for the manufacture of methanol. Journal of Cleaner Production. 2013 Oct;57:19-37.

3. Alvarado M. The changing face of the global methanol industry. IHS Chemical Bulletin. 2016(3):10-1.

4. Liu K, Song C, Subramani V. Hydrogen and syngas production and purification technologies. John Wiley & Sons; 2009.

5. Rase HF. Handbook of commercial catalysts: heterogeneous catalysts. CRC press; 2000.

6. Hu YH, Ruckenstein E. Catalytic conversion of methane to synthesis gas by partial oxidation and CO 2 reforming. Advances in catalysis. 2004;48:297-345.

7. Rostrup-Nielsen JR. aew aspects of syngas production and use. Catalysis Today. 2000 December 25,;63(2):159-64.

8. Spath PL, Dayton DC. Preliminary Screening -- Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas. 2003 /12/01.

9. Song CS. Tri-reforming: A new process concept for effective conversion and utilization of CO2 in flue gas from electric power plants. ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY; AMER CHEMICAL SOC 1155 16TH ST, NW, WASHINGTON, DC 20036 USA; 2000.

10. Ruckenstein E, Hu YH. Combination of CO2 reforming and partial oxidation of methane over NiO/MgO solid solution catalysts. Ind Eng Chem Res. 1998;37(5):1744-7.

11. Noureldin MM, Elbashir NO, El-Halwagi MM. Optimization and selection of reforming approaches for syngas generation from natural/shale gas. Ind Eng Chem Res. 2013;53(5):1841-55.

12. Challiwala MS, Ghouri MM, Linke P, El-Halwagi MM, Elbashir NO. A combined thermo-kinetic analysis of various methane reforming technologies: Comparison with dry reforming. Journal of CO2 Utilization. 2017;17:99-111.

13. Julián-Durán LM, Ortiz-Espinoza AP, El-Halwagi MM, Jiménez-Gutiérrez A. Techno-economic assessment and environmental impact of shale gas alternatives to methanol. ACS Sustainable Chemistry & Engineering. 2014;2(10):2338-44.

14. Minutillo M, Perna A. A novel approach for treatment of CO.sub.2 from fossil fired power plants, Part A: The integrated systems ITRPP. International Journal of Hydrogen Energy. 2009 May 1,;34(9):4014.

15. Minutillo M, Perna A. A novel approach for treatment of CO 2 from fossil fired power plants. Part B: The energy suitability of integrated tri-reforming power plants (ITRPPs) for methanol production. International Journal of Hydrogen Energy. 2010;35(13):7012-20.

16. Ng K, Zhang N, Sadhukhan J. Techno-economic analysis of polygeneration systems with carbon capture and storage and CO2 reuse. Chemical Engineering Journal. 2013 Mar 1,;219:96-108.

17. Zhang Y, Cruz J, Zhang S, Lou HH, Benson TJ. Process simulation and optimization of methanol production coupled to tri-reforming process. International Journal of Hydrogen Energy. 2013 Oct;38(31):13617-30.

18. Dwivedi A, Gudi R, Biswas P. An improved tri-reforming based methanol production process for enhanced CO2 valorization. Int J Hydrogen Energy. 2017;42(36):23227-41.

19. Nowak P, Lachowska M, Skrzypek J. Influence of water vapour on methanol synthesis over CuO-ZnO-Al2O3 catalyst. Chemical Engineering Science. 1991 January 1,;46(12):3324-5.

20. Kung HH, Liu G, Willcox D. EFFECT OF CO2 AND H2O IN THE METHANOL SYNTHESIS REACTION ON Cu-Zn-O. ; 1984.

21. BARDET R, THIVOLLECAZAT J, TRAMBOUZE Y. METHANOLIZATION UNDER PRESSURE OF CARBON OXIDES AND THEIR MIXTURE ON CU-ZN-AL2O3 CATALYSTS-ROLE OF CARBON-DIOXIDE. ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY; AMER CHEMICAL SOC 1155 16TH ST, NW, WASHINGTON, DC 20036; 1984.

22. Naber JD, Siebers DL, Di Julio SS, Westbrook CK. Effects of natural gas composition on ignition delay under diesel conditions. Combust Flame. 1994;99(2):192-200.

23. Smith AR, Klosek J. A review of air separation technologies and their integration with energy conversion processes. Fuel Process Technol. 2001;70(2):115-34.

24. Rostrup-Nielsen JR. Activity of nickel catalysts for steam reforming of hydrocarbons. Journal of Catalysis. 1973;31(2):173-99.

25. Cheng W. Methanol production and use. CRC Press; 1994.

26. Kéromnès A, Metcalfe WK, Heufer KA, Donohoe N, Das AK, Sung C, et al. An experimental and detailed chemical kinetic modeling study of hydrogen and syngas mixture oxidation at elevated pressures. Combustion and Flame. 2013 June 1,;160(6):995-1011.

27. Vernon PD, Green ML, Cheetham AK, Ashcroft AT. Partial oxidation of methane to synthesis gas. Catalysis Letters. 1990;6(2):181-6.

28. York AP, Xiao T, Green ML. Brief overview of the partial oxidation of methane to synthesis gas. Topics in Catalysis. 2003;22(3-4):345-58.

29. Even though many studies have been conducted to investigate steam reforming, dry methane reforming, only a few have considered combination of these two processes. Avci, investigated the reaction of steam reforming of methane. Optimal Design and Decision for Combined Steam Reforming Process with Dry Methane Reforming to Reuse CO2 as a Raw Material. Ind Eng Chem Res. 2012;51(13):4982-9.

30. Lee S. Methanol synthesis technology. CRC Press; 1989.

31. Olah GA, Goeppert A, Prakash GS. Beyond oil and gas: the methanol economy. John Wiley & Sons; 2011.

32. Meyers RA, Meyers RA. Handbook of petrochemicals production processes. McGraw-Hill Prof Med/Tech; 2005.

33. Petrochemical Processes Handbook 2014. Hydrocarbon Processing. 2014 May 1,.

34. Klerk Ad. Fischer-Tropsch Refining. John Wiley & Sons; 2012.

35. Stryjek R, Vera JH. PRSV: An improved Peng—Robinson equation of state for pure compounds and mixtures. The canadian journal of chemical engineering. 1986;64(2):323-33.

36. Stryjek R_, Vera JH. PRSV—An improved peng-Robinson equation of state with new mixing rules for strongly nonideal mixtures. The Canadian Journal of Chemical Engineering. 1986;64(2):334-40.

37. Pellegrini LA, Soave G, Gamba S, Langè S. Economic analysis of a combined energy–methanol production plant. Applied Energy. 2011 December 1,;88(12):4891-7.

38. Chen L, Jiang Q, Song Z, Posarac D. Optimization of methanol yield from a Lurgi reactor. Chem Eng Technol. 2011;34(5):817-22.

39. El-Halwagi MM. Sustainable design through process integration: fundamentals and applications to industrial pollution prevention, resource conservation, and profitability enhancement. Butterworth-Heinemann; 2017.

40. Sinnott RK, Towler G. Chemical Engineering Design: SI edition. Elsevier; 2009.

41. Maqbool W, Lee ES. Syngas Production Process Development and Economic Evaluation for Gas-to-Liquid Applications. Chem Eng Technol. 2014;37(6):995-1001.

42. Gangadharan P, Kanchi KC, Lou HH. Evaluation of the economic and environmental impact of combining dry reforming with steam reforming of methane. Chemical Engineering Research and Design. 2012 November 1,;90(11):1956-68.

43. Ehlinger VM, Gabriel KJ, Noureldin MM, El-Halwagi MM. Process design and integration of shale gas to methanol. ACS Sustainable Chemistry & Engineering. 2013;2(1):30-7.

44. Van-Dal ES, Bouallou C. Design and simulation of a methanol production plant from CO.sub.2 hydrogenation. Journal of Cleaner Production. 2013 Oct 15,;57:38.

45. David J, Herzog H. The cost of carbon capture. fifth international conference on greenhouse gas control technologies, Cairns, Australia; ; 2000.

46. Śliwińska A, Burchart-Korol D, Smoliński A. Environmental life cycle assessment of methanol and electricity co-production system based on coal gasification technology. Sci Total Environ. 2017;574:1571-9.

47. Baranzini A, Goldemberg J, Speck S. A future for carbon taxes. Ecol Econ. 2000;32(3):395-412.

APPENDIX

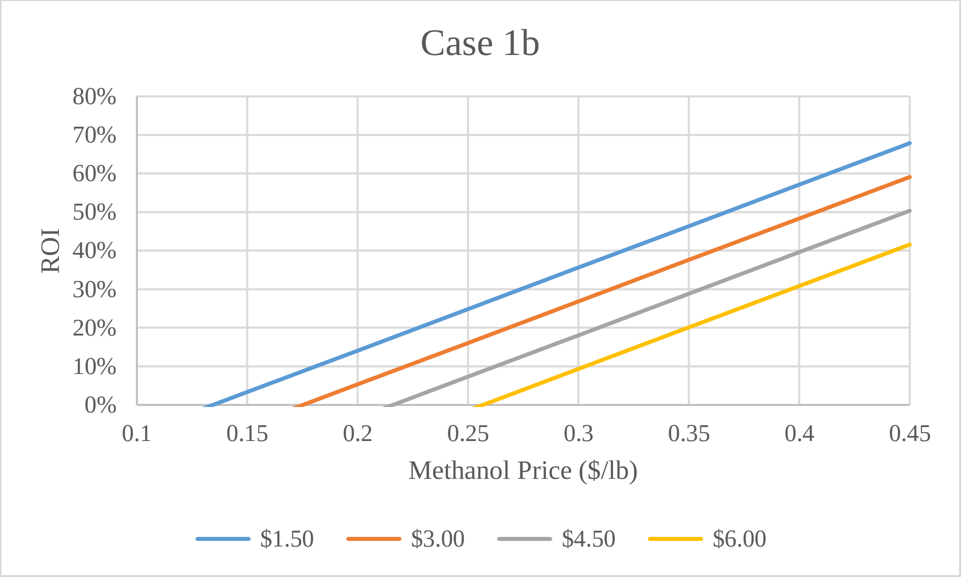


Figure 25 Case 1b sensitivity analysis

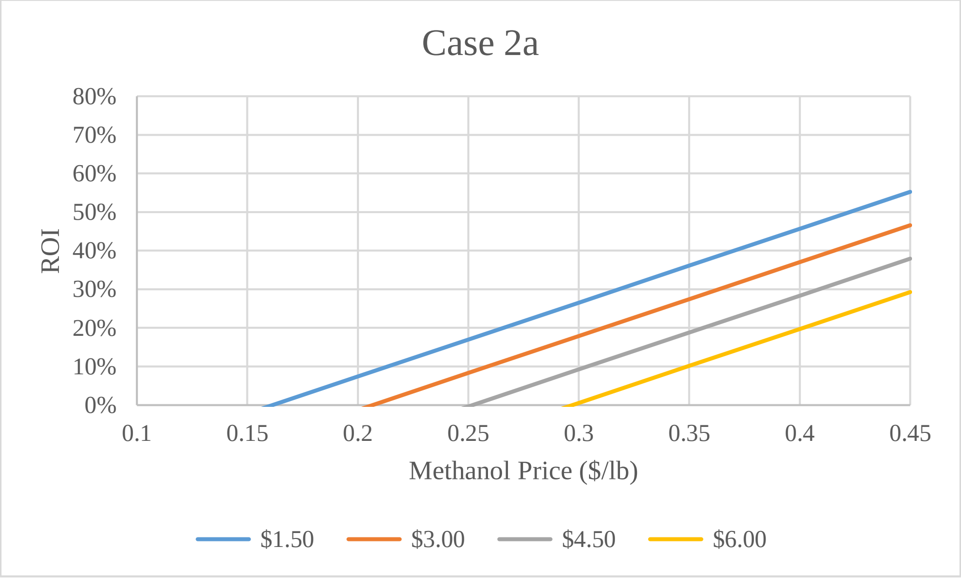


Figure 26 Case 2a sensitivity analysis

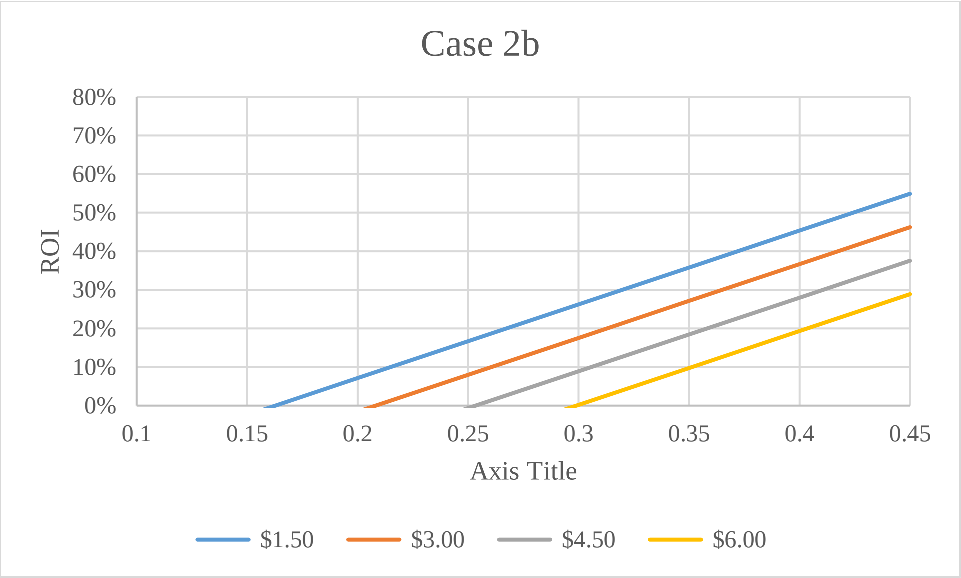


Figure 27 Case 2b sensitivity analysis

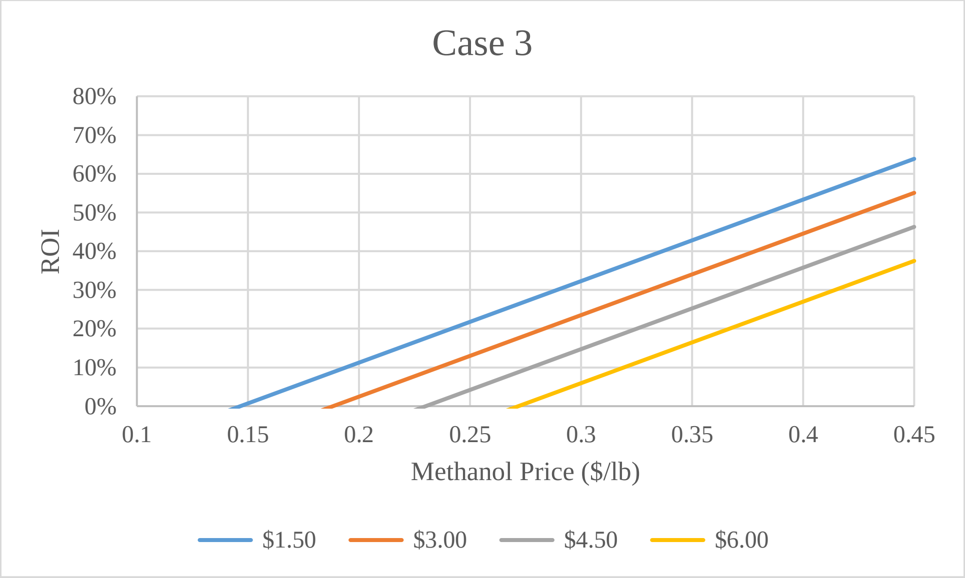


Figure 28 Case 3 sensitivity analysis

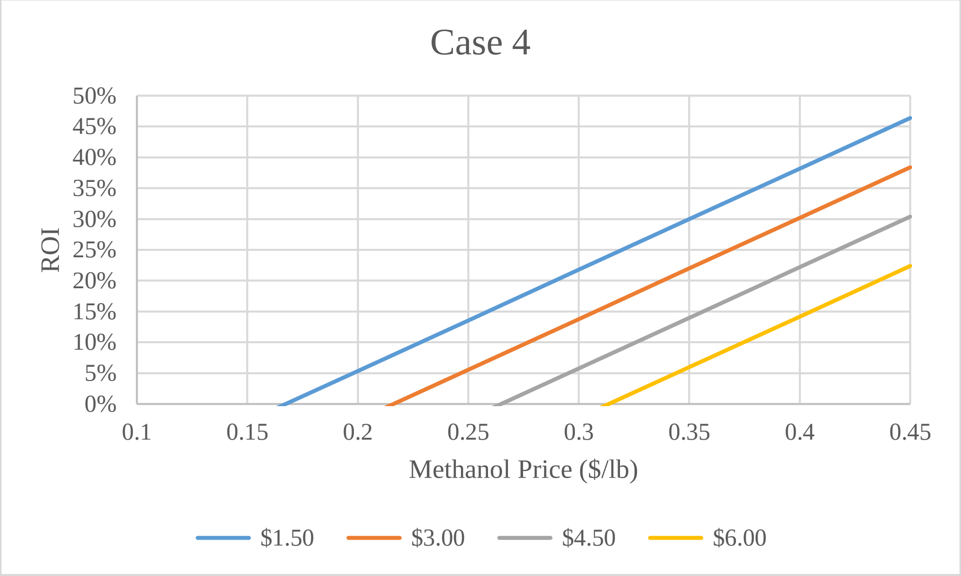


Figure 29 Case 4 sensitivity analysis

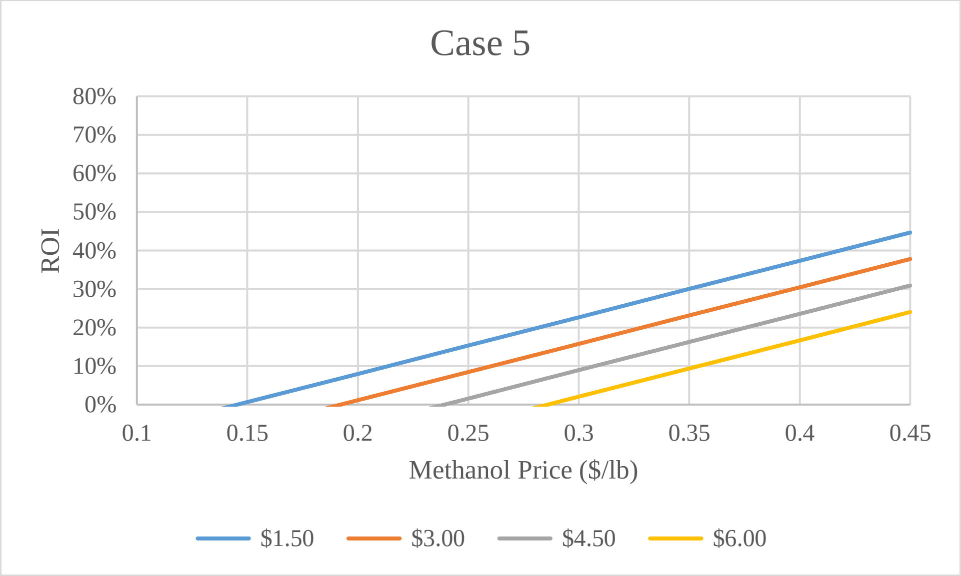


Figure 30 Case 5 sensitivity analysis

Figure 31 Case 6 sensitivity analysis